



NBS TECHNICAL NOTE 543

Electrochemical Analysis Section:

Summary of Activities
July 1969 to June 1970

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Electrochemical Analysis Section: Summary of Activities—July 1969 to June 1970

Richard A. Durst, Editor

Electrochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234



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FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 60 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. We plan to issue these summaries for all of our sections. The following is the sixth annual report on progress of the Electrochemical Analysis Section:

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the sixth annual progress report of the Electrochemical Analysis Section of the Analytical Chemistry Division. It covers the fiscal year 1970, which began on July 1, 1969 and ended on June 30, 1970. This report summarizes the total program of the Section, incomplete studies as well as finished work, and stresses its relationship to the missions of the Division and the Institute.

This Section broadly concerns itself with studies of ionic processes in solution using electroanalytical and other related techniques. During this year, some redirection and reemphasis of effort were undertaken in order to bring the Section expertise to bear on important analytical problems in several areas of science, medicine, and technology. As a result, much of the earlier work of the Section, such as studies of solute-solvent interactions in mixed solvents, has had to be reduced. The special interests of the members of the Section lie for the most part in solution electrochemistry including the competence areas of potentiometry, electrometric titrations, coulometry, and conductometric analysis.

Several changes occurred in the Section staff in the past year which maintained an overall scientific effort of about four man-years. The most significant staff change was the retirement of Dr. Roger G. Bates, who directed the Section since its inception. Dr. Bates, who won international recognition for his studies of hydrogen ion activities and pH scales in addition to his general interests in electrolyte solution thermodynamics and electrode reactions, has accepted the post of professor of Chemistry at the University of Florida. Dr. Bates will remain associated with the Section in the capacity of Consultant.

In order to specify the procedures adequately, it has been necessary in certain instances to identify commercial materials and equipment in this report. In no case does such identification

imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

The support of the Scientific Apparatus Makers Association (SAMA) for ionic activity studies and the U. S. Army Research and Development Command (under Contract No. MOD-9913) for biologic fluid studies is gratefully acknowledged.

Richard A. Durst, Acting Chief
Electrochemical Analysis Section

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ELECTROCHEMICAL ANALYSIS SECTION: SUMMARY OF ACTIVITIES
JULY 1969 TO JUNE 1970

Edited by Richard A. Durst

This survey of the activities of the Electrochemical Analysis Section, Analytical Chemistry Division, covers the period from July 1969 to June 1970. An attempt is made to briefly summarize a year's progress on the technical projects of the Section, to indicate the composition and capabilities of the unit as a whole, and to stress the Section's role in the mission of the Institute. Summaries of the work in each of the Section competences are given. In the area of acidity measurements, work continued on the standardization of tris(hydroxymethyl)aminomethane for use as a biologic pH buffer material and standard for clinical pH measurements. Progress toward reference standards for the calibration of ion-selective electrodes is reported including pM and pCl values for both NaCl and KCl. A study using the silver sulfide ion-selective electrode for measuring trace silver ion losses due to adsorption on selected surfaces is described. High-precision coulometry is used to determine the atomic weight of zinc, the purity of EDTA, and the stoichiometry of gallium arsenide.

Key words: Acidity; conductivity; coulometric analysis; electrochemical analysis; ionic activity; ion-selective electrodes; pH measurements; potentiometry; standard reference materials.

1. INTRODUCTION

For the most part, this has been a year of change for the Electrochemical Analysis Section, both in terms of staff and of mission emphasis. Generally speaking, the changes in Section activities are primarily the result of the opportunity to apply Section expertise in electroanalytical chemistry to help solve a variety of analytical problems in many diverse areas, from biomedicine to solid-state materials.

Examples of this type of involvement can be best illustrated by citing two outside grants for support of Section activities.

In one study, a two-year program on ion-selective electrodes was started under the sponsorship of the Scientific Apparatus Makers Association (SAMA) and the NBS Office of Standard Reference Materials (OSRM), the purpose of this study being to standardize techniques and to prepare high quality reference materials, in order to facilitate the applications of ion-selective electrodes. In brief, this Section will (1) correlate theoretical thermodynamic data with experimental studies of commercial electrodes and evaluate the liquid junction errors; (2) define the ionic activities in solutions of the reference materials; and (3) establish a self-consistent set of activity scales for these ions. The long-range goal is the acquisition, certification, and issuance of standard reference materials for the calibration of ion-selective electrodes.

The other study, supported by a grant from the U. S. Army Medical Research and Development Command, is concerned with the development of methods and materials for studying the behavior of electrolytes in biologic fluids. Specifically, this program was established to develop methods for electrochemically monitoring ion concentrations and gas tensions, and to develop standard materials for calibrating the electrodes used in the

continuous monitoring of ions and dissolved gases in various body fluids. One study being made in this program is the standardization of a new reference material for biologic pH measurements. The glass pH electrode has long demonstrated its utility as a rapid and accurate index of the acid-base balance of biologic fluids and, for the purpose of standardization, NBS had certified a special ratio of its phosphate buffer for the physiologically important range of pH 7 to 8. However, this buffer has certain undesirable characteristics for biologic studies, for example, the phosphate interacts with certain components of body fluids such as calcium and magnesium. For this reason, many biological scientists merely used the NBS phosphate buffer to standardize a more compatible buffer material. To overcome this shortcoming, work is in progress to certify the tris/tris·HCl system [tris = tris(hydroxymethyl)aminomethane] as a new physiologic pH buffer in pure water and in isotonic saline and other synthetic biologic fluids.

In addition to this pH standard, ionic activity standards developed under the SAMA/OSRM grant should also find use in applying ion-selective electrodes to biologic studies. Standards for sodium, potassium, chloride, calcium, etc., will eventually be certified in various mixed electrolyte systems of physiologic importance. In summary, although ion-selective electrodes are extremely promising sensors for biomedical research and clinical medicine, they are nevertheless incapable of yielding accurate and meaningful data until they are adjusted to standard reference activity scales in media of specified composition.

Another area where one of our electroanalytical competences will advance the state of the art is in the accurate determination of the stoichiometry of various semiconductor materials such as gallium arsenide. As a participant in an international characterization exchange coordinated by CECD (Organization for

Economic Cooperation and Development), it is expected that our expertise in coulometric analysis will permit the determination of the stoichiometry of gallium arsenide to an accuracy and precision unattainable by any other analytical technique. Similar studies will be made on high-purity KCl where it is expected that the chloride content can be determined coulometrically with an imprecision of only a few parts per million. The results of these studies will enable participating countries to assess their competence in those aspects of materials science which are of importance for the future development of their industries. Also, these studies will enable correlations to be made between the composition and structure of materials and their bulk properties.

During this year, another contribution to the advancement of the state of the art of ion-selective electrodes was achieved with the publication of the book, "Ion-Selective Electrodes" [1] by the Government Printing Office. This NBS Special Publication 314 is the formal report of the proceedings of the Symposium on Ion-Selective Electrodes held at NBS in January 1969. This volume contains a review of ion-selective electrodes, emphasizing the non-glass types, and provides a thorough and critical evaluation of the subject. It consists of eleven invited review papers (Table 1) and selected discussions from the Symposium. Both the present status and future potential of these sensors are discussed in a wide range of scientific disciplines, from the physical sciences to biomedicine, and extensive bibliographies provide an excellent survey of the literature for anyone using or anticipating the use of these electrodes. Some indication of the interest in this topic can be gained from the fact that, in the first six months that this publication has been available, the entire first printing of 4,000 copies was sold out, and the book has gone into its second printing for use in both the laboratory and the classroom.

Table 1. Table of Contents - "Ion-Selective Electrodes".

Theory of Membrane Electrode Potentials: An Examination of the Parameters Determining the Selectivity of Solid and Liquid Ion Exchangers and of Neutral Ion-Sequestering Molecules

George Eisenman
U.C.L.A.

Solid-State and Liquid Membrane Ion-Selective Electrodes

James W. Ross, Jr.
Orion Research, Inc.

Heterogeneous Membrane Electrodes

Arthur K. Covington
University of Newcastle-upon-Tyne, England

Reference Electrodes

Arthur K. Covington
University of Newcastle-upon-Tyne, England

Thermodynamic Studies

James N. Butler
Tyco Laboratories, Inc.

Activity Standards for Ion-Selective Electrodes

Roger G. Bates and Marinus Alfenaar
National Bureau of Standards

Studies with Ion-Exchange Calcium Electrodes in Biological Fluids: Some Applications in Biomedical Research and Clinical Medicine

Edward W. Moore
Lemuel Shattuck Hospital

Table 1. (Cont'd)

Ion-Selective Electrodes in Biomedical Research

Raja N. Khuri

American University of Beirut, Lebanon

Analytical Studies on Ion-Selective Electrodes

Garry A. Rechnitz

State University of New York at Buffalo

Industrial Analysis and Control with Ion-Selective Electrodes

Truman S. Light

The Foxboro Company

Analytical Techniques and Applications of Ion-Selective Electrodes

Richard A. Durst

National Bureau of Standards

Symposium Discussion

(R. A. Durst)

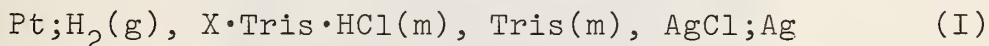
2. ACIDIMETRIC MEASUREMENTS

A. Tris in Water

Tris(hydroxymethyl)aminomethane is being widely used as a biological buffer. The dissociation constant of the protonated form has been determined by emf measurements from 0 to 50 °C and the pK_a at 25 °C is 8.075 [2]. This indicates that tris buffer solutions are suitable for pH measurement and control between pH 7 and 9.

In order to match the pH of a tris buffer solution as closely as possible with the acidity range found in blood and at the same time have a buffer with sufficiently large buffer capacity, the conventional pa_H values of several buffer solutions containing various ratios of protonated and free base were determined.

The method used followed closely the procedure for assignment of pH(S) values to NBS primary pH reference buffers. Emf measurements of the cell (shown in Figure 1)



where m refers to molality and X (the ratio of tris·HCl to tris) was varied from 1 to 4, were made at 5, 25, 37, and 50 °C. The cell solutions were made up by dissolving the free crystalline base in standard hydrochloric acid. The acidity function $p(a_H\gamma_{Cl^-})$ was derived from the measured emf of the cell with the aid of the equation

$$p(a_H\gamma_{Cl^-}) = \frac{E-E^\circ}{k} + \log m_{Cl^-} \quad (1)$$

where E° is the standard emf of the cell [3] and k is $(RT \ln 10)/F$. Conventional pa_H values for each buffer solution were computed by the equation

$$pa_H = (pa_H\gamma_{Cl^-}) + \log \gamma_{Cl^-} \quad (2)$$

where the single ionic activity coefficient for the chloride ion was estimated by the Bates-Guggenheim convention [4]

$$-\log \gamma_{\text{Cl}^-} = \frac{AI^{1/2}}{1+1.5 I^{1/2}} \quad (3)$$

where A is the Debye-Hückel slope and I the total ionic strength.

The buffer value β was determined by the method proposed by Van Slyke [5] which involves the titration of the buffer solution either with a strong base or acid.

The calculated $\text{p}a_{\text{H}}$ values at 25 and 37 °C and the buffer values are listed in Table 2.

The internal agreement of these $\text{p}a_{\text{H}}$ values with the pH scale defined by NBS primary pH standards was investigated by intercomparing the tris buffer solutions with the standard 0.025m phosphate buffer solution having pH(S) 6.862 and 6.838 at 25 and 37 °C, respectively.



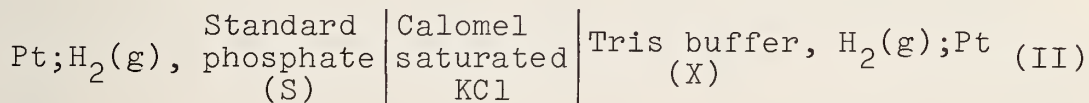
Figure 1. Emf cell (hydrogen vs. silver/silver chloride) for studies of pH buffer solutions.

Table 2. Conventional p_{aH} and buffer values for several tris·HCl/tris buffer ratios.

Tris·HCl/tris	Molality tris·HCl	p_{aH}		Δ^a	β
		25 °C	37 °C		
1	0.02	8.144	7.826	-0.022	0.019
	.05	8.176	7.858	- .039	.054
	.10	8.206	7.888	-	-
3	.02	7.668	7.350	- .026	.012
	.05	7.698	7.380	- .041	.020
	.10	7.727	7.410	-	-
3.5	.02	7.599	7.280	- .025	.010
	.05	7.631	7.313	- .039	-
	.10	7.661	7.343	-	-
4	.02	7.543	7.225	-	-
	.05	7.573	7.254	-	-
	.10	7.603	7.284	-	-

$^a\Delta = pH(X) - p_{aH}$ at 25 °C (residual liquid-junction error).

The cell used was



where the vertical line denotes a liquid junction. The operational pH values of tris buffer solutions were calculated by the equation

$$pH(X) = pH(S) + \frac{E_X - E_S}{k} \quad (4)$$

where E_X and E_S are the potential differences between the calomel and hydrogen electrodes. The differences between the operational pH and corresponding p_{aH} values given also in Table 2 indicate the error caused by liquid junction potential.

The results of Table 2 suggest that the tris buffer solution containing 0.02m Tris·HCl in a ratio of 3 to 1 of the protonated base to free base could be used for pH standardiza-

tion purposes since it has a pH value very close to that of blood, a relatively small liquid junction error, and a sufficient buffer capacity.

B. Buffers in Isotonic Saline

In the course of searching for secondary pH standards in media of biomedical importance, isotonic saline was the first medium selected for study. It consists of 0.16m sodium chloride solution in water and thus simulates blood very closely with respect to its osmotic pressure (and ionic strength).

Electrochemical studies of five buffer systems were made in isotonic saline. The buffers studied were

	<u>Molality</u>
Tris·HCl (m) + Tris (m)	0.005 - 0.16
Bis-tris·HCl (m) + Bis-tris ^a (m)	.01 - .16
Acetic acid (m) + Sodium acetate (m)	.01 - .15
KH ₂ PO ₄ (m) + Na ₂ HPO ₄ (m)	.005 - .035
KH ₂ Citrate (m)	.01 - .12

Emf measurements were made with Cell I containing hydrogen and silver-silver chloride electrodes over the temperature range from 5 to 50 °C. In each case enough sodium chloride was added to the buffer solutions to make the total ionic strength equal to 0.16. From the emf measurements, conventional p_{a_H} values for the buffer mixtures in isotonic saline were determined by the method outlined in the previous section (equations 1-3). Results for selected buffer solutions at 25 °C are given in Table 3.

The comparison of conventional p_{a_H} values in isotonic saline with corresponding values in water at the same buffer concentrations [6-9] in Figure 2 illustrates the neutral salt effect caused by lowering of the activity coefficients of the ionized buffer species by the addition of sodium chloride.

^aBis-tris = 2,2-bis(hydroxymethyl)-2,2',2''-nitrilotriethanol.

Table 3. Conventional p_{aH} values for buffer solutions in isotonic saline at 25 °C.

	Molality				
	<u>0.01</u>	<u>0.025</u>	<u>0.05</u>	<u>0.10</u>	<u>0.16</u>
Tris	8.221	8.224	8.225	8.226	8.228
Bis-tris	6.645	6.646	6.647	6.651	6.656
Acetate	4.637	4.636	4.637	4.639	-
Phosphate	6.770	6.789	-	-	-
Citrate	3.709	-	3.683	3.683	-

As predicted by the Debye-Hückel equation, the p_{aH} is raised for the two amine buffers (tris and bis-tris) and lowered for the two buffers made up either of a neutral weak acid (acetic) or of an anion acid ($H_2PO_4^-$) and their respective salts. By extrapolating the p_{aH} for tris and bis-tris buffers in water [6-9] to ionic strength equal to 0.16, p_{aH} values calculated were 8.229 and 6.653, respectively. They agree within 0.005 units with the corresponding p_{aH} values found in isotonic saline, 8.228 for tris and 6.656 for bis-tris.

The approximate dissociation constants for acetic acid, dihydrogen phosphate ion, and protonated forms of tris and bis-tris in isotonic saline were calculated from the emf measurements with the use of the mass law and the Debye-Hückel limiting law. The ion size parameter was assumed to be zero and the equations used were:

for acetic acid

$$pK'_a = \frac{E-E^\circ}{k} + \log m_{Cl^-} + \log \frac{m_{AcOH}}{m_{AcO^-}} \quad (5)$$

for dihydrogen phosphate ion

$$pK'_2 = \frac{E-E^\circ}{k} + \log m_{Cl^-} + \log \frac{m_{H_2PO_4^-}}{m_{HPO_4^{2-}}} + 2A\sqrt{I} \quad (6)$$

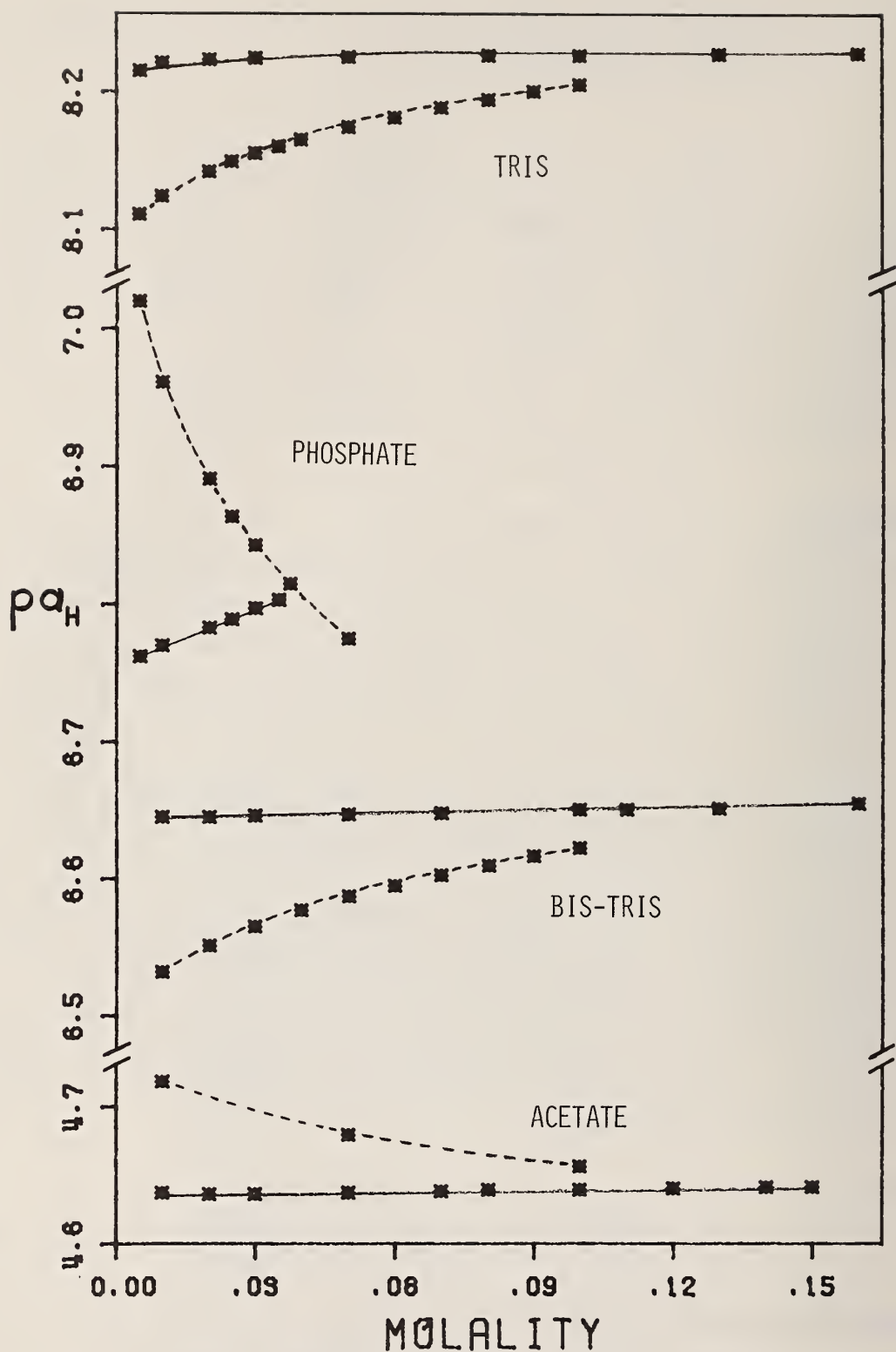


Figure 2. Comparison of conventional $p a_H$ values for buffers in isotonic saline (solid line) and in water (broken line) at 25 °C [6-9].

and for protonated tris and bis-tris

$$pK'_a = \frac{E-E^o}{k} + \log m_{Cl^-} + \frac{m_{BH^+}}{m_B} - 2A\sqrt{I} \quad (7)$$

The results are given in Table 4.

Table 4. The approximate dissociation constants for four acids in isotonic saline at 25 °C.

<u>m</u>	AcOH <u>pK'_a</u>	H ₂ PO ₄ ⁻ <u>pK'₂</u>	Tris·H ⁺ <u>pK'_a</u>	Bis-tris·H ⁺ <u>pK'_a</u>
0.01	4.765	7.306	7.939	6.364
.02	4.764	7.319	7.942	6.365
.03	4.764	7.333	7.943	6.366
.05	4.765	-	7.944	6.366
.10	4.766	-	7.945	6.370
.16	-	-	7.946	6.375

C. Tris in Isotonic Saline

The method used for determining the best buffer composition of tris·HCl and tris in water was followed very closely in isotonic saline. The results are summarized in Table 5.

Table 5. Conventional p_{aH} and buffer values for tris·HCl/tris buffer ratios in isotonic saline solution.

<u>Tris·HCl/tris</u>	<u>Molality tris·HCl</u>	<u>p_{aH}</u>		<u>Δ^a</u>	<u>β</u>
		<u>25 °C</u>	<u>37 °C</u>		
1	0.01	8.220	7.904	-0.048	0.012
	.05	8.225	7.908	- .052	.058
	.10	8.226	7.909	- .057	.112
3	.02	7.745	7.428	- .048	.010
	.05	7.745	7.427	- .049	.026
	.10	7.745	7.430	- .052	.060
3.5	.02	7.678	7.361	- .049	.008
	.05	7.680	7.363	- .053	.028
	.10	7.680	7.363	- .057	.052

^aΔ = pH-p_{aH} at 25 °C.

(M. Paabo)

D. Dissociation of Protonated Tris(hydroxymethyl)aminomethane in Aqueous Alcoholic Solvents

In a previous report [10], the continuing study of acid-base behavior in mixed aqueous solvents was reported. The dissociation constant of the protonated form of tris(hydroxymethyl)aminomethane was determined in 50 weight-percent alcohol-water solvents by means of a potentiometric titration.

This procedure, utilizing an electrochemical cell without liquid junction, was used to extend the investigation to alcohol-water mixtures containing the same mole fraction of alcohol (0.2811) which yielded a better basis for comparing the ion-solvent interactions. A mole fraction of 0.2811 corresponds to the 50 weight-percent point for the ethanol-water solvent.

The following cell was used:

Glass electrode; HCl (0.01m) + tris in
0.281 mole fraction alcohol-water, AgCl;Ag (III)

The initial emf (E_1) was measured at equilibrium before any tris had been added. Successive additions of a solution 0.01m in HCl and 0.1m in tris (m = molal) in the alcohol-water solvent under study led to emf values designated E_2 . In this way, both E_1 and E_2 were determined at a constant chloride molality and a constant total ionic strength, while the buffer ratio (tris/tris·HCl) was changed.

The activity coefficient term in the expression for pK is of such form as to be negligible in dilute solutions [11]; hence, a close approximation to the pK is obtained from the equation

$$pK = \frac{(E_2 - E_1)}{(RT \ln 10)/F} + \log \frac{m_{BH^+}}{0.01m_B} \quad (8)$$

where m_{BH^+} and m_B are respectively the molalities of protonated tris and the free tris base in the solution for which E_2 was measured.

A comparison of results on the weight-percent basis and on the mole-fraction basis is shown in Table 6.

Table 6. Dissociation constants of tris in several alcohol-water mixtures.

<u>Alcohol</u>	<u>pK (in 50 wt-% alcohol)</u>	<u>pK (in 0.2811 mole fraction alcohol)</u>
Methanol	7.799	7.945
Ethanol	7.675	7.675
n-Propanol	7.780	7.815
t-Butanol	7.758	7.730

Whereas the dissociation constants of tris in 50 weight-percent alcohol-water mixtures showed no discernible linear relation to the number of carbon atoms in the alcohol, Figure 3 illustrates that the pK exhibits an almost linear dependence on the number of carbon atoms in the series, except ethanol.

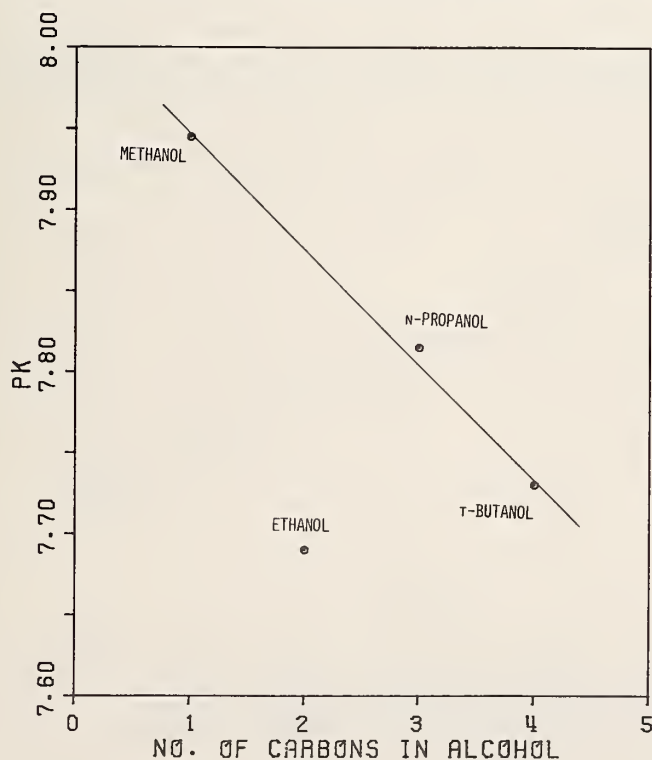


Figure 3. Dissociation constants of tris vs. alcohol carbon number in 0.2811 mole fraction alcohol.

Figures 4, 5, and 6 illustrate the relationship of the pK to the solvent properties density, dielectric constant, and viscosity, respectively.

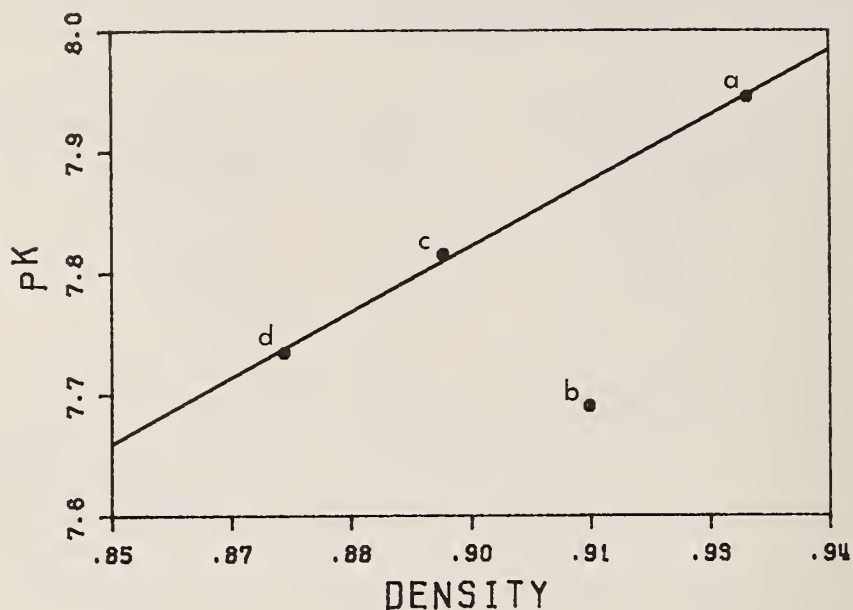


Figure 4. Dissociation constant of tris vs. solvent density; a) methanol, b) ethanol, c) n-propanol, d) t-butanol.

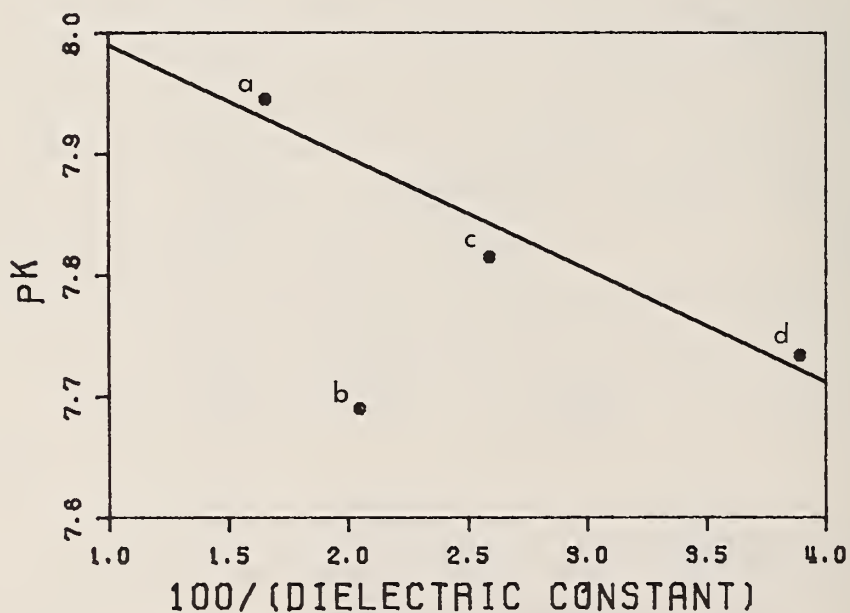


Figure 5. Dissociation constant of tris vs. solvent dielectric constant; a) methanol, b) ethanol, c) n-propanol, d) t-butanol.

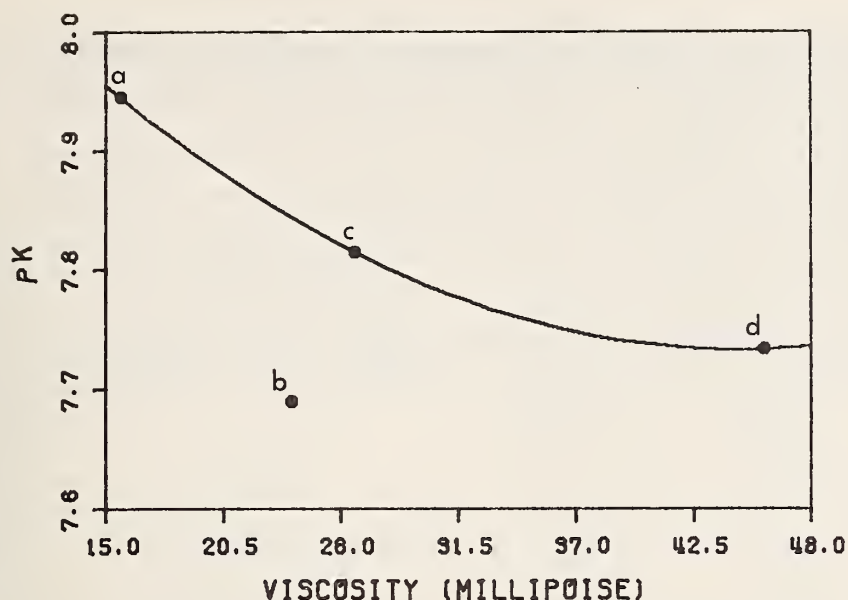


Figure 6. Dissociation constant of tris vs. solvent viscosity; a) methanol, b) ethanol, c) n-propanol, d) t-butanol.

In solvents which contain the same mole fraction of alcohol, the observed trend in pK as a function of the type of alcohol indicates that the major influence on the acid-base behavior of the tris may be the solvent structure. Apparently the higher degree of hydrogen bonding occurring in ethanol-water is responsible for the larger dissociation constant (smaller pK) in that solvent.

On the basis of electrostatic effects, Figure 3 shows a reasonably linear relationship which would indicate that the Fuoss [12] model applies for these alcohol-water mixtures.

$$\log K = \log K^{\circ} + 0.4343b \quad (9)$$

where

$$b = \frac{e^2}{a\epsilon kT}; \quad (10)$$

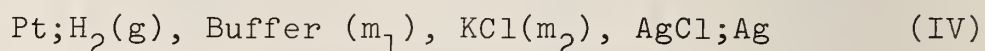
e is the charge on the electron, a is the distance of closest approach of the ions, ϵ is the dielectric constant, k is the Boltzmann constant, and T is the thermodynamic temperature.

(B. R. Staples)

E. Certification of Disodium Hydrogen Phosphate (SRM 186 IIc)

The National Bureau of Standards recently acquired a new lot of disodium hydrogen phosphate to be issued together with potassium dihydrogen phosphate (SRM 186 Ic) as a primary Standard Reference Material for pH measurements. Since minor variation of pH between different lots of material may occur, the pH(S) values of the phosphate buffer solutions were re-determined by a method used previously in this laboratory [13].

The emf of the cell



was measured for buffer solutions containing three different molalities of potassium chloride ($m_2 = 0.005, 0.01, \text{ and } 0.015 \text{ mol kg}^{-1}$) over the temperature range 0 to 50 °C.

The measured emf of this cell, together with the standard emf, was used to calculate the acidity function $p(a_{\text{H}}\gamma_{\text{Cl}})$. The limiting value of the latter $p(a_{\text{H}}\gamma_{\text{Cl}})^\circ$ at zero concentration of added chloride was obtained by least-square extrapolation.

Conventional pa_{H} values were computed using the equation

$$\text{pa}_{\text{H}} = p(a_{\text{H}}\gamma_{\text{Cl}})^\circ + \log \gamma_{\text{Cl}} \quad (11)$$

where the single ionic activity coefficient for the chloride ion was defined by the Bates-Guggenheim convention (Eq. 3).

Three runs were made with the buffer containing 0.025m of each of the phosphates and three runs with the buffer containing 0.008695m potassium hydrogen phosphate and 0.03043m disodium hydrogen phosphate. In addition, the recommendation of practical standardization of the silver-silver chloride electrode in 0.01m hydrochloric acid was followed [14]. Emf measurements at 25 °C gave an E° of 0.22259V (average of 21 cells) for the silver-silver chloride electrode. This represents a difference of 0.25 mV from the Bates and Bower E° value [3]. The same correction was applied to calculations

at all temperatures and the resulting pH values for the two standard phosphate solutions are given in Table 7.

Table 7. pH values for standard phosphate buffer solutions.

t, °C	0.025m KH_2PO_4 0.025m Na_2HPO_4 (average of 3 runs)	0.008695m KH_2PO_4 0.03043m Na_2HPO_4		
		Set I	Set II	Average
0	(6.982) ^a	(7.535) ^a	7.533	7.534
5	6.949	7.502	7.500	7.501
10	6.921	7.474	7.471	7.472
15	6.898	7.451	7.447	7.449
20	6.878	7.431	7.428	7.430
25	6.863	7.416	7.415	7.415
30	6.851	7.404	7.401	7.403
35	6.842	7.395	7.394	7.394
40	6.836	7.389	7.388	7.388
45	6.832	7.385	7.385	7.385
50	6.831	7.384	7.385	7.384
55	6.831	-	-	-
60	(6.834) ^a	-	-	-

^aValues in parentheses obtained by extrapolation.

However, when determined independently here in the same laboratory, the E° values from emf measurements in 0.01m HCl were in such good agreement (i.e., fell well within the standard deviations) at 0° and 50° with the Bates and Bower calculated values, that these calculated values were taken as the E° in an independent determination of pH on the 1:3.5 ratio phosphate buffer solution. The comparison of pH values by two independent determinations, each using an E° consistent with their own experimental values, is well within any experimental error as illustrated in Table 7 (Sets I and II).

(M. Paabo and B. R. Staples)

F. Certification of Borax (SRM 187b)

A new lot of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) to be issued as a primary Standard Reference Material for pH measurements is being certified by the established procedure [13] outlined above. The preliminary values of pH for this material are shown in Table 8.

Table 8. pH values for standard borax buffer solutions.

<u>t, °C</u>	<u>pH (0.01m borax)^a</u>		
	<u>Run I</u>	<u>Run II</u>	<u>Average</u>
0	9.460	9.460	9.460
5	9.391	9.393	9.392
10	9.330	9.332	9.331
15	9.275	9.278	9.277
20	9.227	9.228	9.227
25	9.182	9.184	9.183
30	9.142	9.144	9.143
35	9.106	9.108	9.107
40	9.073	9.075	9.074
45	9.044	9.045	9.045
50	9.015	9.018	9.017

^aAverage Δ (Run II—Run I) = 0.002 pH.

(B. R. Staples)

3. ION-SELECTIVE ELECTRODES

A. Introduction

A continuing program has been underway for several years at NBS to provide a new series of Standard Reference Materials for the calibration of ion-selective electrodes. This program has been designed to meet the practical needs for standardization in many areas, both scientific and industrial, in which these sensors have demonstrated an extremely wide range of application.

Although the response of an ion-selective electrode to a particular ion depends on the activity of that ion in solution, the thermodynamic activity of a single ionic species is not uniquely defined. Recently it was proposed [15] that the convention on which activity standards for ion-selective electrodes are based be made consistent with the existing pH convention. This convention, intended for use at ionic strengths of 0.1 or less, was reasonable under the same limitations as the pH convention. In more concentrated solutions, however, differences between the mean activity coefficients of uni-univalent electrolytes become more pronounced and it appeared that an extension of the simple form of the pH convention was not entirely justified. However, it is possible to establish a conventional scale of activity for a single ionic species by choosing an arbitrary scale for the activity coefficient of that ion. Rather than selecting an entirely arbitrary scale for single ion activity coefficients, the NBS approach to a conventional single ion activity scale is being based on the physical concept of hydration of ions in solution [16]. A cooperative effort between NBS and Dr. Roger G. Bates (University of Florida, Gainesville) and Dr. R. A. Robinson (State University of New York at Binghamton) has resulted in the presently advocated convention [17] based on the Stokes-Robinson hydration theory.

Stokes and Robinson [16] have derived the equation

$$\ln \gamma_{\pm} = |Z_+ Z_-| \ln f_{DH} - \frac{h}{v} \ln a_w - \ln [1 + 0.018(v-h)m] \quad (12)$$

where f_{DH} is the electrostatic contribution expressed as an activity coefficient on the mole fraction scale, a_w is the water activity, v , the number of ions produced by one molecule of the electrolyte, h , is the hydration number and m , the molality.

In this manner, a conventional method, based on a physical theory, of dividing mean activity coefficients into their ionic components forms the basis of the NBS scales of ionic activities.

B. Single Ionic Activity Coefficients

By assuming that the chloride ion is unhydrated [16,17], the hydration theory can be used as a means of dividing the mean activity coefficients of unassociated chlorides into single ionic components. This is a non-thermodynamic assumption, but, unlike many conventions which are highly arbitrary in nature, references provide considerable evidence to support this assumption. Equation (12) rests on two assumptions: a) that water bound to one or both species of ions is no longer a part of the bulk solvent, and b) that the Debye-Hückel expression correctly gives the true activity coefficient (mole fraction scale) of the solvated ions:

$$\ln f_{DH} = \frac{-AI^{1/2}}{1 + B\bar{a}I^{1/2}} \quad (13)$$

In Eq. (13), A and B are constants of the Debye-Hückel theory, $\bar{a}$ is an ion-size parameter, and I is the ionic strength in molarity units (mol l^{-1}).

C. Uni-Univalent Chlorides

From the Gibbs-Duhem equation, the activity of an electrolyte MCl of molality m , is given by

$$-(55.51/m) \, d\ln a_w = d\ln(\gamma_{M^+}^m) + d\ln a_{Cl^-} \quad (14)$$

If the cation is hydrated with h molecules of water and m' is its molality in moles per kilogram of unbound water,

$$m' = \frac{m}{1-0.018hm} \quad (15)$$

and hence

$$\begin{aligned} -(55.51/m') \, d\ln a_w &= -(55.51/m) \, d\ln a_w + h d\ln a_w \\ &= d\ln(\gamma_{M^+}^{m'}) + d\ln a_{Cl^-} \end{aligned} \quad (16)$$

The activity of chloride ion is the same on the two scales: $m\gamma_{Cl^-} = m'\gamma_{Cl^-}'$. From Eqs. (14) and (16),

$$d\ln(\gamma_{M^+}^m) + h d\ln a_w = d\ln(\gamma_{M^+}^{m'}) \quad (17)$$

or

$$\ln \gamma_{M^+} = \ln \gamma_{M^+}' - h \ln a_w - \ln(1-0.018hm) \quad (18)$$

It follows from the postulates of the Stokes-Robinson hydration treatment that the activity coefficient of the hydrated species i on the mole fraction scale is correctly given in terms of Eq. (13) by $\ln f_i = z_i^2 \ln f_{DH}$. Hence, since $v=2$,

$$\ln \gamma_{M^+}' = \ln f_{DH} - \ln[1-0.018(2)m'] \quad (19)$$

and it follows from Eqs. (15), (18), and (19) that

$$\ln \gamma_{M^+} = \ln f_{DH} - h \ln a_w - \ln[1-0.018(2-h)m] \quad (20)$$

Combination of Eq. (20) with Eq. (12) for the mean activity coefficient of a 1:1 electrolyte and with the definition of the osmotic coefficient ϕ

$$\phi = \frac{-\ln a_w}{0.018vm} \quad (21)$$

gives

$$\ln (\gamma_{M^+}/\gamma_{\pm}) = -(h/2) \ln a_w = 0.018hm\phi \quad (22)$$

or

$$\log \gamma_{M^+} = \log \gamma_{\pm} + 0.00782hm\phi \quad (23)$$

from which

$$\log \gamma_{Cl^-} = \log \gamma_{\pm} - 0.00782hm\phi \quad (24)$$

D. Alkaline Earth Chlorides. For an unassociated salt MCl_2 , the same procedures lead to

$$\ln \gamma_{M^{++}} = 4 \ln f_{DH} - h \ln a_w - \ln [1+0.018(3-h)m] \quad (25)$$

from which

$$\log \gamma_{M^{++}} = 2 \log \gamma_{\pm} + 0.00782hm\phi + \log [1+0.018(3-h)m] \quad (26)$$

$$\text{Since } 3 \log \gamma_{\pm} = \log \gamma_{M^{++}} + 2 \log \gamma_{Cl^-},$$

$$2 \log \gamma_{Cl^-} = \log \gamma_{\pm} - 0.00782hm\phi - \log [1+0.018(3-h)m] \quad (27)$$

E. Equipment

A slight modification in the measuring system has been adopted. A digital voltmeter, DVM, accurate to 0.01 mV has been integrated into the system and is being used to directly measure the potential of most of the electrode systems except those of very high impedance, such as the glass electrodes.

In the case involving high impedance, the DVM is used to measure the output of a vibrating reed electrometer. The measuring system, complete with temperature controlling instruments, is shown in Figure 7.

F. Procedure for Conventional Single Ionic Activities

A procedure for determining values of single ionic activities, based on the hydration theory, is described. The mean activity coefficients $\gamma_{\pm}$ are obtained from Robinson and Stokes [18] and NBS Report 9908 [19]. They are first fitted as a function of molality by computer calculation. In the

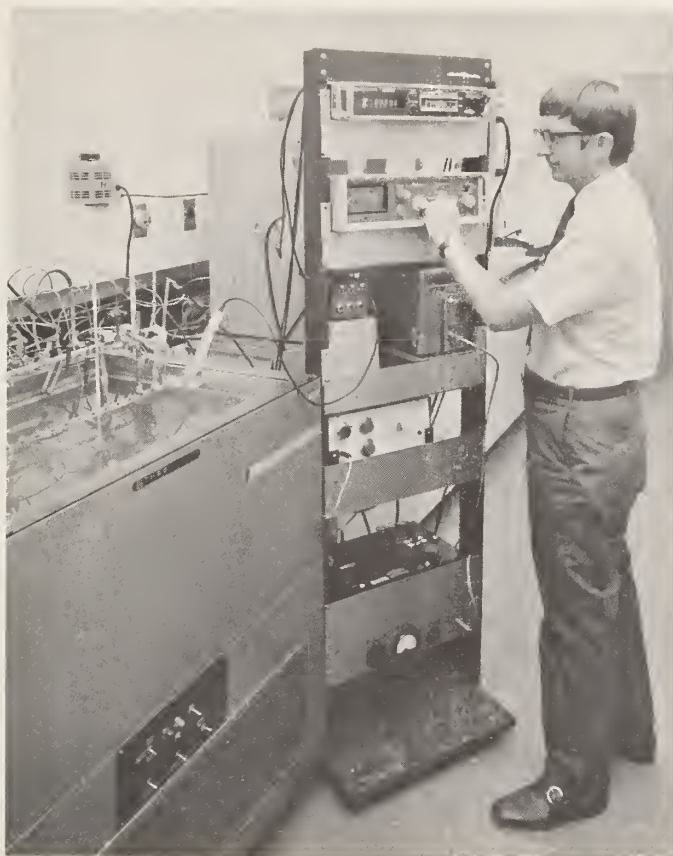


Figure 7. Equipment for measurement of ion-selective electrode cell emf.

same manner, the osmotic coefficient is obtained as a function of molality.

When the data are available, as in the case of NaCl and KCl, at different temperatures, the activity and osmotic coefficients may be expressed as a function of the temperature at particular molalities.

To obtain the molarity, M , the function M/m is expressed as a function of molality, hence, the molarity can be shown at various molalities.

The hydration theory [Eq. (24)] is then used to compute $\log \gamma_+$ and $\log \gamma_-$ the single ionic activity coefficients of

the cation and anion, respectively, then the activities are easily obtained by

$$\log a_i = \log \gamma_i + \log m_i \quad \text{or} \quad a_i = \gamma_i m_i \quad (28)$$

The resulting pM and pCl values are shown in Table 9, along with other pertinent results, which illustrate some of the information that will appear on forthcoming SRM certifications for ion-selective electrode standards (NaCl). Table 10 appears in the following Section concerning KCl standards for ion-selective electrodes.

G. Activity Standards for Ion-Selective Electrodes

A number of sodium, potassium and chloride ion-selective electrodes, obtained from various manufacturers, were compared for Nernstian response. All electrodes checked were found to respond "ideally" within an estimated experimental error of about 0.6-0.8 percent of the theoretical slope at temperatures of 10, 25, and 40 °C.

High quality NaCl and KCl have been obtained from commercial sources and have been certified for homogeneity, purity, and single ionic activities. The results for the activity standards for Na^+ and Cl^- , based on the hydration theory [17], are illustrated in Table 9, and for K^+ and Cl^- , in Table 10.

Table 9. Activity standards for sodium chloride

Molality (m)	Molarity (M)	Activity (cation)	γ_+	Activity (anion)	γ_-	pNa	pCl
0.001	0.000997	0.000965	0.965	0.000965	0.965	3.015	3.015
.01	.00997	.00903	.903	.00902	.902	2.044	2.045
.1	.0995	.0783	.783	.0773	.773	1.106	1.112
.2	.1987	.148	.744	.145	.727	0.828	0.838
.3	.2975	.216	.721	.209	.697	.664	.680
.5	.4941	.350	.701	.331	.662	.455	.480
1.0	.9789	.696	.696	.620	.620	.157	.208
1.5	1.4543	1.077	.718	.904	.602	-	.044
2.0	1.9200	1.504	.752	1.187	.593	-	-

Table 10. Activity standards for potassium chloride

<u>Molality (m)</u>	<u>Molarity (M)</u>	<u>Activity (cation)</u>	<u>γ_+</u>	<u>Activity (anion)</u>	<u>γ_-</u>	<u>pK</u>	<u>pCl</u>
0.001	0.000997	0.000965	0.965	0.000965	0.965	3.016	3.016
.01	.00997	.00901	.901	.00901	.901	2.045	2.045
.1	.0994	.0772	.772	.0768	.768	1.112	1.115
.2	.1983	.145	.723	.143	.713	0.841	0.846
.3	.2967	.208	.693	.204	.680	.682	.690
.5	.4916	.330	.659	.320	.639	.482	.495
1.0	.9692	.623	.623	.586	.586	.206	.232
1.5	1.4329	.917	.611	.836	.558	.0376	.078
2.0	1.8827	1.219	.609	1.077	.539	-	-

(B. R. Staples)

4. POTENTIOMETRY

Ion-Selective Electrode Study of Trace Silver Ion Adsorption on Selected Surfaces

A. Introduction

The adsorption of low concentrations of silver ion on container surfaces has been recognized and evaluated by radio-tracer and chemical methods for some time, as demonstrated for example in the study of the bacteriological and chemical behavior of silver [20,21]. This effect has recently been under systematic reinvestigation using the radioactive silver tracer method for a wide variety of materials and conditions [22,23]. These investigations were designed to give estimates of the amounts of ions lost by adsorption to various surfaces and to determine the most suitable storage containers and conditions for water samples containing low levels of silver. In these studies, silver adsorption as high as 140 percent (on Pyrex at the 50-ppb silver level) was reported. It was shown by autoradiography that such high adsorption levels are apparently due to inhomogeneity of silver adsorption on the surfaces, i.e., the calculation of the total percentage adsorption from the measured specific adsorption assumes uniform silver adsorption which, in fact, does not occur [23].

By making silver ion-selective electrode measurements of the solution rather than the container surface, it should be possible to avoid the uncertainties caused by non-uniform adsorption. That is, instead of measuring a specific surface area which may or may not be representative of the actual degree of adsorption, the electrode senses an "average" ionized silver level which is homogeneous and represents the difference between the original amount of silver present and the total amount adsorbed.

Additional advantages are realized in the potentiometric method by the reduction of experimental complexity, both in equipment and methodology. Measurement techniques analogous

to pH determinations are used without recourse to radioactive tracers and daily isotope (^{111}Ag) decay corrections or to multiple sets of solutions and containers. The use of a single set of containers and solutions further eliminates uncertainties due to differences in surface characteristics of the vessels.

B. Experimental

Silver stock solutions were prepared from reagent grade silver nitrate without further purification. Emf measurements were taken with a silver sulfide ion-selective electrode in conjunction with a double-junction reference electrode. The emf readout was made to the nearest 0.1 mV using a recorder connected to the output of an expanded scale pH/mV meter.

The container materials tested in this study were: Pyrex, Vycor, polyethylene, Teflon (FEP), and Pyrex coated with Desicote (Beckman Instruments, Inc.).

Stock solutions were made by dissolving weighed amounts of silver nitrate in distilled water, with no added inert electrolytes or complexing ligands. All solutions in this study were approximately neutral and no attempt was made to study the effect of pH on adsorption. From the stock solution (10^{-4}M), several electrode-calibration solutions between 10^{-4} and 10^{-7}M were made by serial dilution. The data obtained from these standard solutions were used to establish the calibration curve shown in Figure 8 which was used to relate the observed emf readings to silver ion concentrations. From a consideration of the calibration curve and the expected levels of adsorption (50 to 80 percent), it was decided to use an initial silver ion concentration of $2 \times 10^{-6}\text{M}$ (~ 0.2 ppm) in the test containers. This level of silver was selected in order that the measured silver concentrations would always be read from a linear portion of the calibration curve where maximum sensitivity is attained, i.e., down to approximately $4 \times 10^{-7}\text{M}$. This was in fact achieved since the highest level of adsorption observed

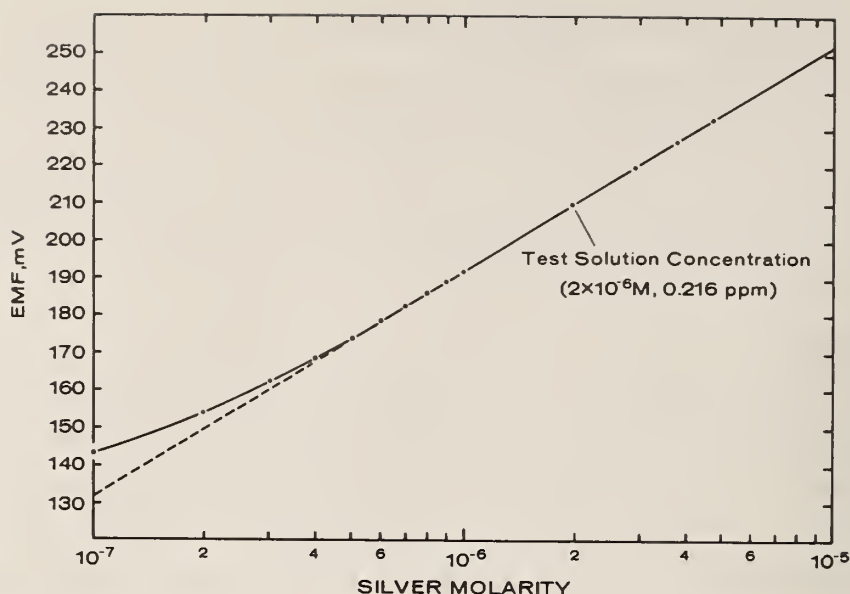


Figure 8. Response of the silver sulfide electrode to silver concentration. Response slope in the linear region of the calibration curve is 59.5mV/pAg (ambient temperature 25 ± 1 °C).

was about 60 percent, corresponding to a silver concentration of 8×10^{-7} M remaining in solution. It should be noted that this silver level (0.2 ppm) is intermediate to those used in the radiotracer studies of West, et al. [22,23] who used silver concentrations at the 0.05 and 1.0-ppm levels.

From another stock solution (2×10^{-4} M AgNO_3), fresh calibration standards were prepared each day with which the electrode system was calibrated before, during, and after each series of measurements on the five test solutions. These three electrode calibration measurements were then plotted against measurement time for an emf-drift correction. A drift-correction factor was then applied to each test solution reading according to its actual measurement time. After correcting for the emf drift which amounted to as much as several millivolts, the silver concentration was read from the calibration curve.

Each of the five different test beakers was washed with dilute detergent solution, rinsed repeatedly with distilled water, and air dried. The standard silver solution ($2 \times 10^{-6}\text{M}$; 0.216 ppm) was then added to each of the clean test beakers. Emf readings were randomly taken of the five test solutions concomitantly with the electrode-calibration measurements, and the emf-drift corrections were applied at the conclusion of each series. A duplicate series was run each day. Over the 46-day span of this study, a total of 56 series was run with the frequency of measurements decreasing toward the end of the period. Between measurements, the test beakers were stored under inverted beakers to prevent both evaporation and contamination by air-borne dust.

The percent adsorption was calculated by the equation:

$$\%_{\text{ads.}} = \frac{\text{Ag}(0) - \text{Ag}(t)}{\text{Ag}(0)} \times 100 \quad (29)$$

where:

$\text{Ag}(0)$ = original silver concentration, $2 \times 10^{-6}\text{M}$; and

$\text{Ag}(t)$ = silver concentration at some time, t , after the introduction of the solution into the test beaker.

Thus, $\text{Ag}(0) - \text{Ag}(t)$ represents the amount of silver removed from solution by adsorption. Because of differences in the sizes of the beakers used and consequently the volumes of silver solution, the surface area-to-volume ratio varied from 0.85 cm^{-1} for Teflon to 0.75 cm^{-1} for other materials. This would, in effect, tend to exaggerate the adsorption values for Teflon by about 10 percent.

C. Results and Discussion

Adsorption percentages calculated by the above equation are shown in Figure 9 for the time period up to 10 days. During this period of the highest adsorption rates, the Pyrex and Desicoted Pyrex containers showed the greatest losses of silver, reaching the 10-15 percent adsorbed levels in the first 24-hour

period. The other three materials adsorbed less, ranging from about 5 percent for polyethylene down to less than 2 percent for Teflon. Note that all of the reported adsorption percentages are mean values with a maximum variability (range) of about 1 percent and an average variability of 0.5 percent.

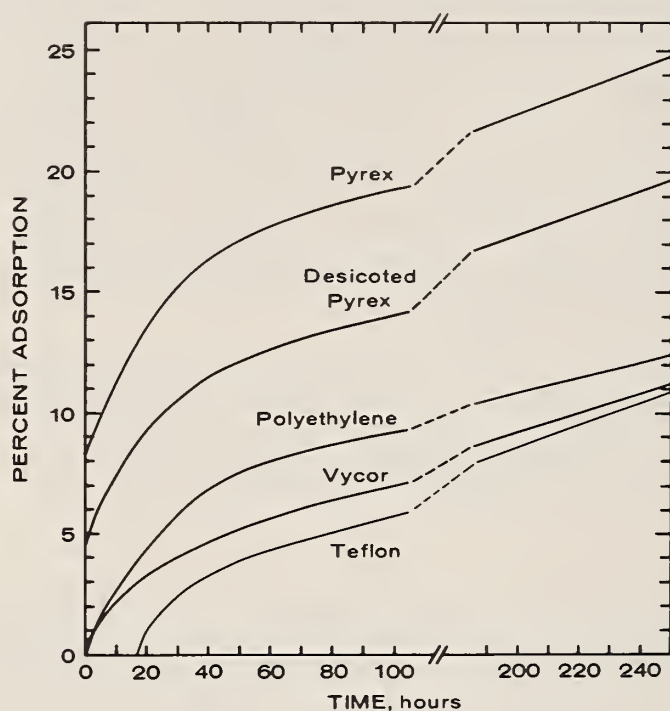


Figure 9. Percent silver adsorption vs. time for five selected materials. Initial silver concentration $2 \times 10^{-6} \text{M}$ (0.216 ppm). Average variability in measurements $\pm 0.5\%$ absolute.

The adsorption percentages for the periods ending 10, 30, and 46 days are summarized in Table 11. Also given in this table are the average adsorption rates for the time intervals between 10, 30, and 46 days.

Table 11. Adsorption percentages^a and rates^b for 0.216 ppm silver solution on various materials.

	10 days	Average $\Delta\%/\Delta t$	30 days	Average $\Delta\%/\Delta t$	46 days
Pyrex	24.5%	1.2	48.0%	0.7	59.5%
Desiccated Pyrex	19.0	1.1	40.5	.7	51.0
Polyethylene	12.0	1.0	32.5	.9	47.0
Vycor	11.0	0.9	28.0	.9	43.0
Teflon (FEP)	10.5	1.1	33.0	1.1	50.0

^ato the nearest 0.5 percent, ^bto the nearest 0.1 percent/day

The table is arranged according to the decreasing degree of adsorption at the end of ten days. This initial order does not hold at the end of 30 and 46 days where both polyethylene and Vycor replace Teflon at the low end of the adsorption scale. From Figure 9, it is evident that the cause of this relationship is the initial induction period (about 18 hours) exhibited by Teflon but not by any of the other materials. Although this effect was noted for Teflon by West et al., they also observed varying degrees of induction for several of the other materials. However, differences in the silver concentration levels make intercomparison of results difficult for these materials.

An interesting trend indicated from Table 11 is that the greatest differences in adsorption between materials occurs at relatively short times, i.e., within 2 or 3 days, and at longer times the rates of adsorption become comparable. Furthermore, as expected, the adsorption rates decrease more rapidly for the materials that adsorbed greatest initially, but the surprising observation is that the degree of adsorption at long times seems to become independent of the surface material. That is, although at 46 days there is still a spread of almost 20 percent (43 to 60 percent) between the maximum (Pyrex) and minimum (Vycor) adsorption values, the average rate of adsorption during the 30 to 46-day period is still 0.9 percent/day

for Vycor but has decreased from 1.2 percent/day to 0.7 percent/day for the Pyrex. This trend more or less holds for all of the materials except Teflon which at 50 percent absorbed is still adsorbing at an average rate of about 1.1 percent/day during the period 30 to 46 days.

In comparison to the values found by West et al. (Table 12), our values for silver adsorption at 10 days tend to be higher (except for Vycor) and our values at 30 days are more consistently low (except for Teflon). The silver adsorption on Vycor at 10 days and on Teflon at 30 days fall within the limits found by the radiotracer method.

Table 12. Silver adsorption by radioactive tracer method of West et al. [22,23]

	10 days		30 days ^a
	<u>0.05 ppm</u>	<u>1.0 ppm</u>	<u>0.05 ppm</u>
Pyrex ^b	2-12%	7-15%	49-140%
Desicoted polypropylene ^c	n.a.	7-9	65-75
Polyethylene ^b	0-5	7-12	40-79
Vycor ^c	2-5	16-18	58-108
Teflon ^c	4-7	2-4	8-44

^adata not available for the 1.0-ppm silver level at 30 days.

^bdata taken from reference [22].

^cdata taken from reference [23].

D. Conclusion

From these electrode studies, Vycor appears to be the best material of those studied in regard to the smallest long-term silver losses due to adsorption. Unfortunately, even these losses are too serious for Vycor to be of use in the storage of dilute silver solutions. For short-term storage, i.e., periods of up to one day, Teflon exhibited silver losses of less than two percent and is adequate for such periods. For storage intervals of more than one day, none of the materials

tested are satisfactory and a chemical stabilizer (complexing ligand) such as thiosulfate [22,23] would appear to be essential.

This study has demonstrated the feasibility of using the silver ion-selective electrode for the direct potentiometric determination of silver in long-term investigations of trace silver adsorption. However, the electrometric method is less suitable than the radiometric method for silver concentrations below the micromolar level and is unusable for "in situ" studies in which complexing ligands have been added. In this latter case, measurements could be made on aliquots taken from the test containers and determined by a standard addition procedure. At the micromolar silver level and above, the electrometric technique offers the advantages of less complex and costly equipment, simplified procedure, and improved precision over the radiometric method.

The electrometric technique could also be used for adsorption studies of other ions, e.g., Cu^{++} , Cd^{++} , Pb^{++} , and F^- , for which ion-selective electrodes are available which perform well down to the 10^{-7} molar level. In addition, simultaneous multiple ion studies, i.e., for preferential adsorption, displacement, and other types of interactions, could be performed using ganged (multiple) ion-selective electrodes. In summary, ion-selective electrodes should prove to be of considerable benefit in the study of trace levels of ions on the basis of the continuous and non-destructive nature of the measurements and also on the sensitivity and precision that can be obtained.

(B. T. Duhart)

5. COULOMETRY

A. Introduction

The long-range goal of the coulometry program is to place chemical characterization, i.e., analytical chemistry, on an absolute basis: to change it from a science of measurement which requires qualifying statements descriptive in nature (such as "based on high purity silver", or "compared to high purity single crystal material") to a science in which the magnitude of the measured property is "based on the values of units of time, mass and length as maintained by the NBS". Much of the coulometry research is geared to achieve this end. The coulometric methods of analysis which are developed at our facility are specifically designed to yield high reproducibility (precision) of the results. The second stage of each research effort entails investigation to test and prove the accuracy (or inaccuracy) of the method. When these two requirements are met (high precision and high accuracy) the method is then adopted for use in such areas as certification of Standard Reference Materials. The developed methods encompass the whole spectrum of chemical reactions: acidimetry, alkalimetry, oxidation-reduction reactions, precipitation reactions and complexometry. Occasionally research in coulometry brings us very close to another area of less applied nature, namely the area of physical constants. Thus, it becomes possible to redetermine by an independent method either the faraday or the atomic weights of various elements. Redetermination of the atomic weight of zinc is one such undertaking.

An area of tremendous interest today is stoichiometry, particularly the stoichiometry of semiconductors. Presently, a concentrated research effort is underway in this very area: determination of the stoichiometry of gallium arsenide.

Several primary standard SRMs were characterized, evaluated and certified in the course of this year via coulometry.

The following section of this report will highlight some of the significant aspects of the activities in coulometry during the past year.

B. Research

1. Coulometry of Zinc

Because elemental zinc is a rather active metal, little, if any, coulometric work was done with the Zn^0 , Zn^{++} couple. Its amphoteric behavior (resulting in spontaneous dissolution either in acid or in alkaline solutions) and insolubility as the hydrous oxide in neutral solutions further detracted from it being considered as a promising element for quantitative electrolysis.

Our initial effort in the electroanalytical chemistry of zinc was made during the investigation of amalgam stripping coulometry as a possible high-precision analytical method. Being such an active metal, zinc appeared to be ideally suited for testing the anodic stripping method. Our expectation at that time was fulfilled: with samples of zinc as small as 7 mg, a precision of 0.01 percent was obtained [24]. The experiment itself, however, offered only the method for determining elemental zinc and perhaps other metals in a sample which could be converted to an amalgam, and could not be applied to the determinations where these metals exist as compounds.

The recovery of zinc could not be evaluated to the desired degree of accuracy since the accepted atomic weight of zinc (65.37) was only known at that time to 0.01 AMU or 0.015 percent, however, the results appeared to be systematically low by about 0.01 percent. Such an error could, of course, result from the "corrosion current" contribution to the overall dissolution of zinc. The source of this error remained temporarily unsolved.

In the meantime, the Bureau acquired and certified 99.9999 percent pure zinc metal (SRM 682) and it became

challenging to test the reason for the observed behavior in the anodic stripping experiments.

A proposal was made and, in collaboration with Professor Robert T. Foley of The American University, investigation of the coulometric behavior of zinc was undertaken.

The Problem: The object of this research is to determine, by an absolute method, the electrochemical equivalent of zinc. The obtained electrochemical equivalent will serve as the basis for a new, independent redetermination of the atomic weight of zinc, which at present is the subject of some controversy. Materials of different origins will be investigated to establish natural variations in the atomic weight of terrestrial zinc.

Significance of the Research: The presently-accepted value for the atomic weight of zinc is 65.37 [25]. The work on the atomic weight of zinc was reevaluated last by the International Commission on Atomic Weights in 1961 [26]. The above value is based primarily on $\text{ZnCl}_2/2\text{Ag}$ [27], $\text{ZnCl}_2/2\text{AgCl}$ [27], ZnBr_2/Zn [28], and ZnCl_2/Zn [29] combining weight ratios. Two mass spectrometric determinations of the isotopic abundances [30,31] yield a significantly different value for the atomic weight of zinc -- 65.387. The Commission, however, recommended retaining the chemically determined value of 65.37. Such a discrepancy in the value of the atomic weight cannot remain unresolved, particularly since for most of the other elements the uncertainties in the atomic weights are of the order of 0.001 AMU, or one order of magnitude less than they are for zinc.

A third, independent, electrochemical method for the determination of the electrochemical equivalent and the atomic weight of zinc is proposed which will aid in resolving the existing discrepancy in this important physical constant.

The suitability of electrochemical methods for the determination of atomic weights was implied in the original work of Faraday. In 1833 he established that the law of definite proportions holds even when the chemical reactions are not carried out directly but are induced by the passage of electric current through the electrolysis cells [32]. The amount of chemical change produced at the electrodes of a cell is directly proportional to the quantity of charge passed. Explicit utilization of Faraday's laws for the determination of atomic weights was recognized very early in the development of quantitative electrochemistry. Thus, for example, Laird and Hulett state [33]:

"Faraday's law, that a definite quantity of electricity is associated with one gram equivalent of any ion, is, as far as we know, strictly accurate, probably as accurate as the law of conservation of mass. There is evidence that not even as small a quantity of electricity as 10^{-16} coulomb passes from an electrolyte to an electrode without a corresponding chemical change taking place..."

Using electrolytic deposition of cadmium in series with a silver coulometer, Laird and Hulett were able to obtain precise Cd/Ag ratios, and assigning a value for the atomic weight of silver they were able to calculate the atomic weight of cadmium. A similar approach was used by Gladstone and Hibbert earlier [34] for the determination of Zn/Ag and Zn/Cu ratios, and consequently, the atomic weight of zinc. Unfortunately, we now know that silver deposition coulometers and copper coulometers, though precise, are not very accurate due to the variation of the amount of occluded mother liquor in the deposit. This aspect of silver deposition coulometers is discussed by W. J. Hamer [35]. A more direct approach to the determination of the electrochemical equivalent is through the use of absolute current and time measurement, employed by D. N. Craig and co-workers [36] in the determination of the electrochemical equivalent of silver and the faraday and by

us in the determination of the electrochemical equivalents of benzoic acid and oxalic acid [37].

The difference between chemical values for the atomic weight of zinc (65.37) and the value obtained mass spectrometrically (65.39) is of the order of 0.03 percent. The anticipated value of the atomic weight obtained by the electrochemical method will have an uncertainty of 0.002 percent (this uncertainty will result primarily from the uncertainty of the faraday: 96487.0 ± 1.6 abs. C/g-equiv). Nonetheless, even this uncertainty is 1.5 orders of magnitude smaller than the existing discrepancy in the atomic weight of zinc. The significance of such an improvement in a physical constant as important as the atomic weight is self-evident.

The Method: The investigation undertaken here entailed the following specific studies which were necessary for accurate evaluation of the electrochemical equivalent and the atomic weight of zinc:

(1) study of the exchange currents and the rate of corrosion of zinc and zinc amalgams in various electrolytes used in the proposed coulometers (Tafel's relationship);

(2) study of the current efficiency as a function of current density for anodic dissolution of zinc;

(3) study of the current efficiency as a function of current density for cathodic deposition of zinc into amalgam;

(4) design, construction and quantitative performance evaluation of anodic zinc coulometer;

(5) design, construction and quantitative performance evaluation of cathodic zinc coulometer;

(6) study of the effects of various parameters on the electrochemical equivalent of reference zinc sample (parameters include current density, current density distribution, impurities in electrolyte, electrolysis time, mass of zinc involved in the reaction and surface area of electrodes);

(7) determination of electrochemical equivalent and atomic weight of zinc using materials of three levels of purity:

(a) NBS Standard Reference Material 682 Zinc - 99.9999 percent,

(b) NBS Standard Reference Material 683 Zinc - 99.999 percent,

(c) commercial zinc - 99.9 percent;

(8) survey of zinc of various origins for possible natural variations in the isotopic composition.

Results: The first stage of research permitted the selection of the optimum electrolyte and electrodes to be used in further studies as well as evaluation of the magnitude of spontaneous corrosion of zinc and zinc amalgam and the corrections for this effect. The need for an inert atmosphere was also resolved here, and the second and third stages of the investigation established optimum current densities to be used in the final coulometric experiments which, if exceeded, would result in oxidation of water to oxygen in the case of the zinc anode, oxidation of mercury in the case of zinc-amalgam anode and reduction of hydrogen ion in the case of zinc or zinc-amalgam cathode.

The fourth and fifth stages involved the design of the apparatus, which permitted accurate measurement of the mass difference for zinc cathodes and anodes involved in the electrochemical reactions. The resistance of coulometers must be sufficiently low to permit the passage of currents up to one ampere (using a 60-V power supply, the resistance must be 60 ohms or less). The coulometric configuration finally used in the experiments is shown in Figure 10.

This configuration of the gravimetric coulometer combines many desirable features. Anodes are suspended freely from a permanently attached support wire, thus no mass transfer takes place as a result of the clamping of the lead wire. Experi-

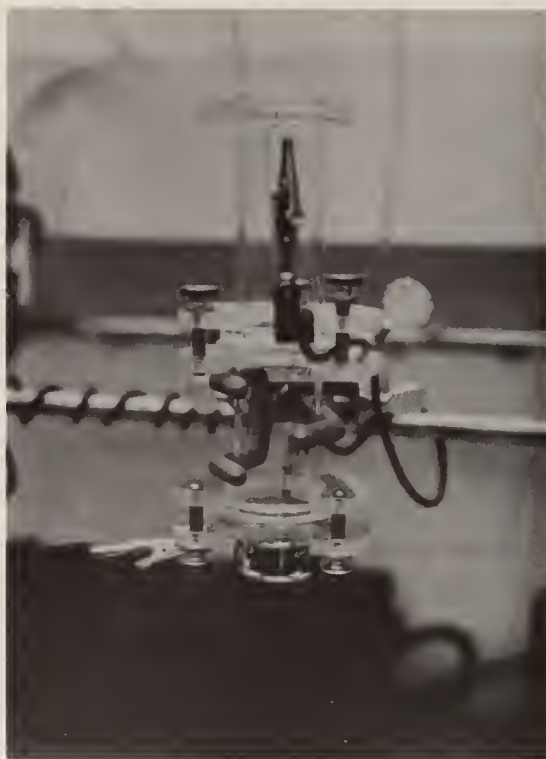


Figure 10. Coulometer for the determination of the atomic weight of zinc.

ments involving the measurement of mass changes of the support wire when large quantities of charge (10^4 coulombs) were passed show no systematic change in its mass. This being the case, there can be no net mass transfer between the support lead and the suspension wire of the zinc anode.

A nitrogen atmosphere can be easily maintained over the solution, thus reducing the rate of spontaneous dissolution of zinc.

The provision of a flat ground-glass joint in the middle of the cell permits the insertion of porous-glass frits or Millipore filters across the cell to determine whether or not there is any physical sedimentation of zinc particles due to deterioration of the anode in the course of dissolution.

Finally, a cup cathode filled with mercury at the bottom of the cell can be used for the gravimetric determination of the zinc deposit.

The sixth stage of the research involved investigation of all possible experimental parameters (other than purity of zinc) on the electrochemical equivalent of one lot of zinc, selected to serve as the reference material.

Although the published results of mass spectrometric investigations indicate no significant variations in the isotopic composition of zinc, nevertheless to insure that the value obtained in this research is truly representative of the terrestrial zinc, an experimental survey of primary zinc-bearing minerals from worldwide sources would be highly desirable. It is hoped to conduct this comparative study on virgin minerals which have not been subjected to metallurgical processing, since the latter could produce isotope separation (isotope separation can occur in such processes as distillation which is commonly used in purification of zinc).

The results of this research are presently being prepared for publication in the appropriate journals. In brief, however, no systematic differences were detected in the electrochemical equivalent of zinc samples originating from various sources. The anodic coulometer with zinc amalgam anode is capable of operating at a high level of precision (standard deviation of a single measurement is 0.002 percent). Oxygen in zinc metal has a significant effect on the electrochemical equivalent, and must be removed (vacuum fusion). The anodic coulometer is unaffected by metallic impurities, as one would expect since only a few metals are more active than zinc. Oxygen in the electrolyte enhances the corrosion of zinc amalgam. In the absence of oxygen the corrosion current density is only 5×10^{-7} A cm⁻². The results of this research permit calculation of the atomic weight of zinc with a 95 percent confidence limit of 0.001 percent.

2. Further Implications of Zn^{++} Generation

a. EDTA analysis. In addition to fundamental interest in the atomic weight of zinc, the electrogenerated zinc ion can be very conveniently used as a reagent for complexometric coulometry. The equilibrium constant for complexation of Zn^{++} with EDTA is about 3×10^{16} , making it highly suitable for coulometric titration of EDTA.

A new coulometric method was developed for EDTA analysis which makes use of amperometric end-point detection under conditions where the indicator signal is proportional to the uncomplexed Zn^{++} concentration. Samples of the disodium salt of EDTA, weighing two grams, were titrated by this method. The preliminary results indicate a highly reproducible titration as shown in Table 13.

The material has not been assayed by another independent method to test the accuracy of these results, but the manufacturer's assay is 99.9 percent.

Table 13. Analysis of $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$.

<u>Sample No.</u>	<u>Assay, percent</u>	<u>Δ, percent</u>
1	99.937 ₈	- 0.0015
2	99.933 ₈	+ .0025
3	99.937 ₂	- .0009
Average	99.936 ₃	

Standard deviation of a single determination:

$$\sigma = 0.0022 \text{ percent}$$

b. Determination of stoichiometry. The newly developed EDTA titration method is applied to the analysis of metals for the purpose of determination of compound stoichiometry. Thus, in the cooperative characterization exchange pro-

gram under the auspices of the Organization for Economic Cooperation and Development (OECD), one of the materials which is studied from the standpoint of its stoichiometry is gallium arsenide (i.e., Ga:As ratio). The determination of gallium is in fact carried out in our laboratory by the EDTA back-titration method.

Coulometric analysis of gallium arsenide stoichiometry is interesting for several reasons. Stoichiometry of semiconductors is in general of interest to the electronics industry because of the dependence of their electrical properties on small deviations in stoichiometry. At present there are no satisfactory methods for this purpose at the required degrees of accuracy and precision. To establish the stoichiometry (or the departure from it) for a 1:1 compound such as GaAs by coulometry, it is not necessary to know the atomic weights of the elements in question. The only prerequisite is to develop 100.000 percent efficient coulometric reactions upon which the measurements of electrochemical equivalents will be based. Once the quantity of electric charge (number of electrons) which is required to carry arsenic in a given sample through a definite chemical change (e.g., $\text{As[III]} \rightarrow \text{As[V]} + 2e$) and gallium in the same sample through a chemical change unique for this element has been determined, stoichiometry can be easily established. It represents merely the ratio of charges consumed in the two independent reactions. Such a determination does not even require accurate mass, current or time measurement as long as these values are the same for the two independent determinations.

If, on the other hand, current, time and mass measurements are made accurately the additional information could be invaluable. First, since arsenic occurs in nature as a monoisotopic element, its atomic weight is known to the nearest 0.0001 AMU (or about 0.0002 percent). The atomic weight of gallium, on the other hand, is known only to the nearest 0.01 AMU. There-

fore, knowing the stoichiometry of GaAs and knowing the sample mass accurately the atomic weight of Ga can be computed from the Ga/GaAs ratio. Furthermore, the atomic weight of Ga can be computed independently from Faraday's law.

Projection into the future promises successful application of this method to such compounds as zinc sulfide, zinc telluride, indium compounds, determination of the ferric ion, analysis of cupric compounds, mercuric compounds and the like.

3. Potassium Dichromate

Potassium dichromate, one of the most commonly used oxidimetric standards has been issued by NBS for a number of years. Exhaustion of the last lot (SRM 136b) and the continuing demand for this standard necessitated its renewal. As with the previous lot, the Office of Standard Reference Materials relies on the coulometric method for absolute standardization of this oxidant.

Twenty subsamples of $K_2Cr_2O_7$, representing a single lot of the material, were analyzed. Thus, each five weight percent of

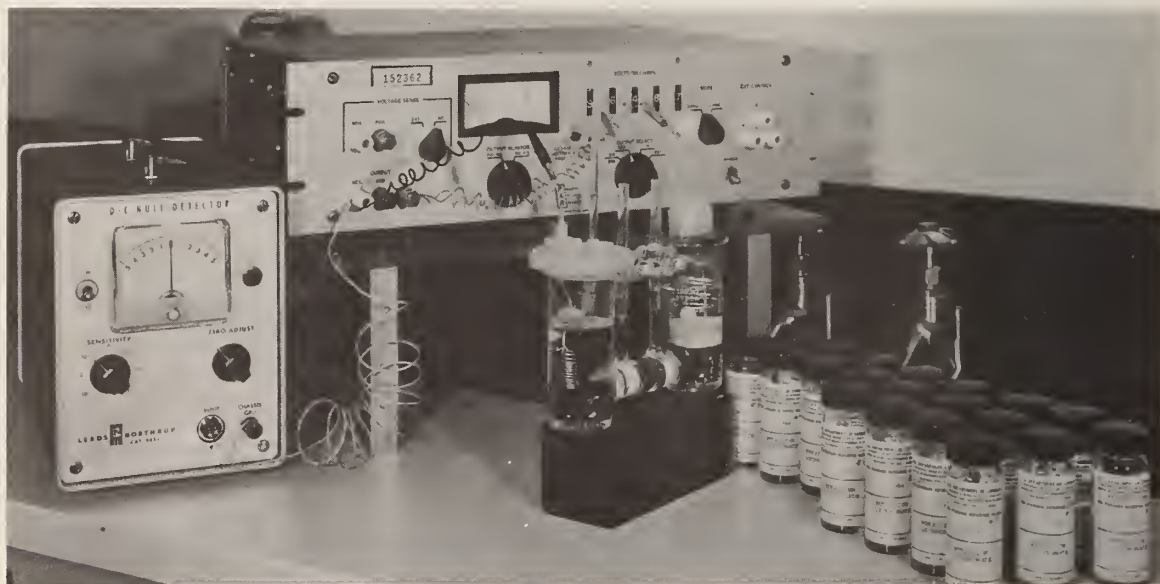


Figure 11. Potassium dichromate samples and some of the coulometric equipment used in standardizing this oxidant.

this lot of the material was tested. Approximately five grams of material were taken from each bottle, dried for six hours at 130 °C in an air atmosphere drying oven, and stored in a P_2O_5 desiccator. One-gram samples (one from each bottle) were weighed out by substitution using standard stainless steel weights (true mass = 0.999901g). The weight of the sample was corrected to true mass by applying appropriate corrections for the buoyancy of air.

Weighed samples were transferred into 125-ml Erlenmeyer flasks and titrated coulometrically in a random sequence over the period of a few weeks by a method developed in this laboratory [38]. The results of analysis are summarized in Table 14.

Table 14. Summary of data of $K_2Cr_2O_7$ analyses.

<u>Titration sequence</u>	<u>Bottle number</u>	<u>Assay, %</u>	<u>Residuals</u>
1	3	99.9849	0.0027
2	19	99.9821	- .0001
3	8	99.9840	.0018
4	10	99.9847	.0025
5	1	99.9797	- .0025
6	11	99.9845	.0023
7	2	99.9790	- .0032
8	17	99.9801	- .0021
9	5	99.9825	.0003
10	20	99.9864	.0042
11	14	99.9874	.0052
12	15	99.9792	- .0030
13	12	99.9786	- .0036
14	6	99.9794	- .0028
15	9	99.9794	- .0028
16	18	99.9825	.0003
17	4	99.9804	- .0018
18	16	99.9863	.0041
19	7	99.9796	- .0026
20	13	<u>99.9833</u>	.0011

Mean 99.9822

$\sigma = 0.0028$

SD of the mean = 0.0006₄

Discussion of the Results: The mean value of the assay of this material is 99.9822 percent. The standard deviation of this mean, based on 19 degrees of freedom, is 0.00064 percent. One can assume that the mean assay of the lot represents the mean of all populations of the twenty arbitrary subdivisions of the lot. The traditional approach to standard reference materials is to ask the following questions. Is this lot of material homogeneous? If so, how accurately is the value of the assay known? What uncertainty should be assigned to the mean which represents the property content of this material? Unfortunately, some of the questions cannot be answered unequivocally. In the following paragraphs, I will attempt to present my views on the subject.

The precision of the analytical method was previously evaluated [38], and the estimate of the standard deviation of a single determination was 0.0029 percent. Since the evaluation of the method was conducted on a single bottle of material, this standard deviation reflects a combination of only two possible distributions: (1) random errors of measurement (σ_m), and (2) within the bottle heterogeneity of material (σ_h).

It is therefore reasonable to express the overall standard deviation as a rms value of the two contribution factors, i.e.:

$$\sigma_{\text{tot}} = \sqrt{\sigma_m^2 + \sigma_h^2} = 0.0029\%. \quad (30)$$

Unfortunately, these two components cannot be evaluated separately without apriori knowledge of either the precision of the method or the heterogeneity of material used to test the method (without varying experimental conditions). Consequently, in evaluating the homogeneity of a given lot of material one can only estimate the difference in between-bottle variability from within-bottle variability. The random fluctuations of composition (within-bottle variability) cannot be separated from the random errors of the method.

The data obtained in this investigation (Table 14) show that between-bottle variability is negligible in comparison with combined within-bottle variability and variability due to the random error component of the method.

$$\sigma_{\text{tot}} = 0.0029\%$$

$$\sigma_{\text{between-bottles}} = 0.0028\%$$

One can therefore treat all of the titration results as samples representing a single population. This random error contribution to the overall uncertainty of the assay at the 95-percent confidence level is

$$\frac{t_{95} \sigma_{\text{tot}}}{\sqrt{n}} = 0.0014\% \quad (31)$$

Let us consider other pertinent data which can shed light on the sample vs. method contribution to the overall error.

In the coulometric measurement process, two types of random errors are involved: (1) errors independent of, and (2) errors dependent on the magnitude of the measured property. These two types of errors can be illustrated by the following example. The charge which is passed through the coulometric cell is equal to

$$Q = \int_0^t I dt. \quad (32)$$

Coulometric titrations are conducted at constant current; however, the word "constant" should really be "virtually constant", since there is always some random fluctuation of current. This current can be subdivided into two parts: time-independent, I° ; and time-dependent, $I(t)$, i.e.,

$$I = I^\circ + I(t) \quad (33)$$

or

$$Q = I^\circ t + \int_0^t I(t) dt. \quad (34)$$

As indicated above in the constant-current mode of operation, it is assumed that

$$\int_0^t I(t) dt = 0 \quad (35)$$

Clearly, this condition is fulfilled if $I(t)$ is a random or periodic function of time and if $t \rightarrow \infty$. Thus, the larger the magnitude of the measured property, requiring longer periods of time, the more nearly is this condition fulfilled. This, then, is magnitude-dependent error.

Moreover, I° is compared to the voltage of the saturated Weston cell as an $I^\circ R$ drop through a standard resistor. In any given experiment, the comparison between this $I^\circ R$ drop and the emf of the Weston cell can be in error by some magnitude ΔI° which is determined by the sensitivity of the comparison system. This error will be time-independent and consequently independent of the magnitude of the property measured. Over a large number of experiments, n , however,

$$\lim_{(n \rightarrow \infty)} \sum_{i=1}^n \Delta I_i^\circ = 0 \quad (36)$$

The errors of type (1) include such things as day-to-day variation of the standard frequency, diurnal variation of the standard resistor, standard cells, air density (in corrections of mass to vacuum), sample transfer losses, etc. Errors of type (2) may include end-point uncertainty, sensitivity of the balance, switching error, etc.

Thus if one plots these two types of errors against sample size, the qualitative graph shown in Figure 12 should be obtained.

The variability of the results due to within-bottle heterogeneity of material will also behave as a type (2) error, since in a given population of crystals the *a priori* probability of any one crystal having a certain amount of the given property is constant.

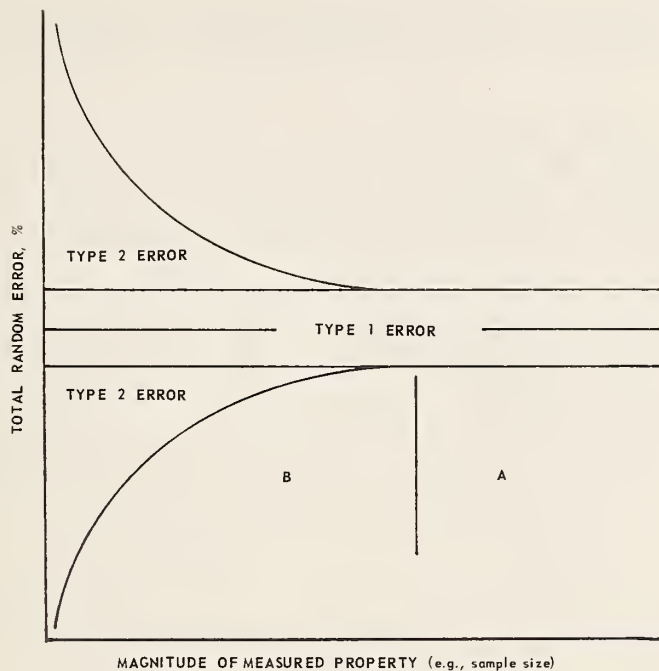


Figure 12. Two types of random errors which are encountered in coulometry

The possibility of the existence of within-bottle variability of material is not unrealistic since the material contains 0.018 percent of inert impurity (assay of 99.982 percent, very low impurity content based on emission spectrum and spark-source mass spectrometric analyses, and slow weight loss on prolonged drying at elevated temperatures indicates possible occlusion of mother liquor in the crystals). Its distribution within the sample need not be uniform since a relatively small number of crystals is taken in any one sample for analysis (e.g., 1-gram sample contains, on the average, 6500 crystals).

If one is working in region B of the error curve it is not possible to separate the method errors from the heterogeneity of material unless 100.00-percent pure material is used to test the method. In the case of "absolutely" pure material, there is no impurity to be distributed and therefore all random errors are due to the method. On the other hand,

even with impure material (99.982 percent), when one is working in region A, the error of type (1) can be attributed only to the method.

Let us, therefore, examine the available data of Tables 14, 15, and 16. These titration results were obtained with 1-g, 0.5-g, and 0.1--0.2-g samples, respectively. The precision of these three sets of data (expressed as the standard deviation of a single determination) is 0.0028 percent, 0.0029 percent, and 0.0030 percent, respectively. Thus, a factor of five change in sample size (6500 crystals in 1-g sample to 1300 in 200-mg sample) changes the precision from 0.0028 to 0.0030 percent, or seven relative percent.

Referring to Figure 12, we must therefore be operating in region A. As indicated above, heterogeneity of material would, of necessity, manifest itself as region B. For this reason, one can conclude that the random error of the analytical results reported here can be ascribed to a large extent to the method uncertainty and not heterogeneity of the material. Such reasoning, then, permits us to separate the random error of the method from within-bottle variability of material.

The analyses of three samples of material on an "as received" basis (not subjected to drying) are shown in Table 17. It is quite clear that the material belongs to the same population as the dried samples.

On the other hand, we have no control over the environment (e.g., humidity) to which the samples will be exposed by the user and for that reason, specification of the drying procedure is warranted as a precautionary measure.

In the overall assessment of data, one can combine the results of Tables 14, 15, and 16 since no significant difference exists between these sets of data. Thus, excluding one outlier from Table 16, the mean assay of the material is

$$99.982 \pm 0.0011\%,$$

where the uncertainty figure represents the 95-percent confi-

Table 15^a. Analysis of $K_2Cr_2O_7$, 136b, (sample size - 0.5g).

<u>Sample Number</u>	<u>Assay</u>				
	<u>Set I</u>	<u>Set II</u>	<u>Set III</u>	<u>Set IV</u>	<u>Set V</u>
1	99.980 ₀	99.975 ₅	99.974 ₂	99.983 ₅	99.978 ₅
2	99.978 ₈	99.973 ₆	99.973 ₄	99.973 ₇	99.977 ₇
3	99.975 ₁	99.973 ₉	99.973 ₅		99.977 ₂
4	99.975 ₇	99.978 ₇	99.974 ₇		99.977 ₁
5	99.978 ₉	99.978 ₃	99.977 ₈		99.976 ₂
6	99.981 ₂	_____	_____	_____	_____
Average	99.978 ₃	99.976 ₀	99.974 ₇	99.978 ₆	99.977 ₃
SD for each set	0.002 ₄	0.002 ₄	0.001 ₈	0.006 ₉	0.000 ₉
	<u>Set VI</u>	<u>Set VII</u>	<u>Set VIII</u>	<u>Set IX</u>	<u>Set X</u>
1	99.976 ₉	99.984 ₆	99.978 ₉	99.978 ₃	99.976 ₀
2	99.976 ₆	99.982 ₀	99.977 ₁	99.978 ₇	99.976 ₉
3	99.977 ₅	99.968 ₅	99.976 ₄	99.976 ₉	
4	99.978 ₄	99.975 ₂	99.978 ₅		
5	99.978 ₇		99.979 ₆		
6	_____	_____	_____	_____	_____
Average	99.977 ₆	99.977 ₆	99.978 ₁	99.978 ₀	99.976 ₅
SD for each set	0.000 ₉	0.006 ₀	0.001 ₃	0.001 ₀	0.000 ₇

Overall average: 99.977₂, $\sigma = 0.002_9$

^aTaken from Reference [38].

Table 16. Analysis of smaller samples of $K_2Cr_2O_7$ (SRM 136c).

<u>Bottle Number</u>	<u>Sample size, g</u>	<u>Assay, %</u>	<u>Residuals</u>
2	0.2	99.9873	0.0031
2	.1	99.9832	- .0010
2	.2	99.9798	- .0044
5	0.2	99.9823	-0.0019
5	.2	99.9882	.0040
5	.2	99.9824	- .0018
12	0.2	99.9686 ^a	
12	.1	99.9840	-0.0002
12	.2	99.9865	.0023
Avg		99.9842	
		$\sigma = 0.0030$	

^aThis result appears to be an outlier. It is excluded from consideration of this set of data.

Table 17. Analysis of $K_2Cr_2O_7$ (SRM 136c) "as received" (1-g samples).

<u>Bottle Number</u>	<u>Assay, %</u>	<u>Residuals</u>
2	99.9802	-0.0032
5	99.9852	+ .0018
12	99.9849	+ .0015
Mean	99.9834	
		$\sigma = 0.0028$

dence interval for the mean based on 30 degrees of freedom.

The accuracy of the result is also dependent on the systematic errors of the determination. The estimate of possible systematic error in these analyses due to uncertainties in molecular weight, faraday, emf standard, resistance standard, and mass standard, is 0.0033 percent.

The overall 95-percent confidence interval is

$$\sigma_{\text{random}} + \sigma_{\text{syst}} = 0.0044\% \quad (37)$$

In certifying a standard, an overly conservative (just as an overly optimistic) assignment of uncertainty limits does disservice to those who use the standard because it, in fact, conceals some of the available information about the standard. Uncertainties must be assigned realistically.

In the case at hand, the estimate of the 95-percent confidence interval for the mean (making allowances for possible systematic errors) was shown to be 0.0044. It would thus appear that 0.005 percent is a realistic estimate of the magnitude of the uncertainty of the mean-measured property (the oxidimetric assay of $\text{K}_2\text{Cr}_2\text{O}_7$).

The above treatment of data and the conclusions drawn on the basis of that treatment are valid, however, they represent a view from a definite, clearly defined standpoint -- the estimate of the uncertainty of the mean property. The uncertainty figure of 0.005 percent refers to the mean property of the whole lot of the material (assuming on the basis of the indications of the limited number of measurements that the heterogeneity of the material is negligible), including the allowances for known possible systematic errors, and the reduced random error of measurement by the well established $\sigma/\sqrt{n}$ treatment due to the natural tendency of random errors (r_i) to distribute normally about zero, so that in the limit

$$\lim_{(n \rightarrow \infty)} \sum_{i=1}^n r_i = 0 \quad (38)$$

An alternate treatment of SRM analytical data which arose in the course of discussions on polycrystalline materials in general can also be applied to $\text{K}_2\text{Cr}_2\text{O}_7$ [39]. This treatment is directed towards probabilistic evaluation not of the mean property of the material itself (i.e., not heterogeneity,

separation of the random errors of the method, etc.), but rather the treatment of material-method-man system performance at the time of the analysis. On the basis of this treatment, a two-sided tolerance limit, Ks , can be assigned to the mean value of the measured property, $\bar{X}$.

Treating the data of Table 14 in this manner where $\gamma = 0.95$ (the probability is 95 percent that at least a proportion P of the distribution is included within $\pm Ks$ limits) and the proportion of the population is also 95 percent (i.e., $P = 0.95$) for sample size $n=20$, $K = 2.752$ and $s = 0.0028$ percent, one can say that the assay of the material (based on the $F = 96486.7 \text{ C}_{\text{US-69}} \text{ equiv}^{-1}$; electrical, frequency, and mass standards as maintained by NBS) is

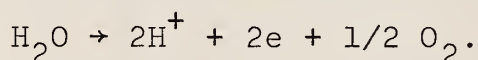
$$99.9822 \pm 0.0077,$$

where the uncertainty figure represents 95 percent probability bounds that at least 95 percent of all measurements on all samples in this lot would fall within these limits, if measured by means of the above instrument-man system.

The results of this work and the work on arsenious oxide analysis are being incorporated into a NBS Monograph (260 series) on the characterization of Redox Standard Reference Materials.

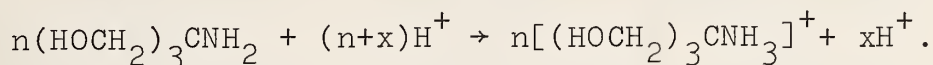
4. Tris - Basimetric Standard

Studies of tris(hydroxymethyl)aminomethane in this laboratory showed that tris cannot be coulometrically titrated directly via the anodic reaction

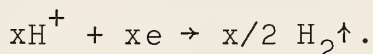


The experimentally determined assay was consistently low by several percent. A systematic survey of the literature from 1947 to the present revealed no attempts to titrate tris coulometrically. Its electrochemical behavior in general has not been investigated. Relevant evidence in the literature shows that attempts to titrate aromatic amines coulometrically failed due to oxidation of the amines themselves.

This difficulty, however, is circumvented by a back-titration procedure which was developed in this laboratory. The following reaction is used for alkalimetric assay of tris.



The coulometric reaction involves only the reduction



Thus, for quantification purposes, the acid solution is standardized coulometrically, then a known amount of the acid is added in excess to preweighed samples of tris and the excess of acid is back-titrated coulometrically.

The material to be issued as a standard reference material arrived in five cases. Fifteen random samples (three from each case) were evaluated. Random sampling and the experimental design furnished by Dr. John Mandel (Statistical Consultant, NBS) were followed. Duplicate titrations were performed on each of the random samples in an experiment consisting of two sets. One sample from each bottle was removed, dried at 70 °C in a vacuum oven for 24 hours, weighed, corrected to weight in vacuum, and titrated. This constitutes Set I. The second set is identical to the first set except the sequence of weighing and titration of samples was altered at random.

Approximately 1.6 molar sulfuric acid solution, standardized coulometrically, was used in these titrations. Back-titration of the excess sulfuric acid was carried out to a differential potentiometric inflection point. In each titration, about one gram of tris and about 5.5 grams of H_2SO_4 solution were used. Using 100 ml of 1M KCl supporting electrolyte and the above amounts of tris and H_2SO_4 , the $(\Delta\text{pH}/\Delta\text{C})_{\text{max}}$ occurred in the vicinity of $\text{pH} = 5$.

The results of analyses are summarized in Table 18. Roman numerals in the Sample Number column indicate the case numbers and Arabic numerals -- the bottle number. The duplicate

Table 18. Results of coulometric analysis of tris - basimetric standard.

<u>Sample Number</u>	<u>First Set</u>	<u>Second Set</u>
I-7	99.9787	99.9559
I-9	99.9683	99.9734
V-6	99.9461	99.9532
IV-6	99.9699	99.9675
III-12	99.9763	99.9707
II-12	99.9810	99.9709
III-11	99.9749	99.9665
V-5	99.9690	99.9754
II-9	99.9641	99.9657
IV-2	99.9841	99.9555
III-4	99.9746	99.9727
V-9	99.9695	99.9689
II-10	99.9645	99.9703
IV-8	99.9685	99.9750
I-2	99.9690	99.9689
Average		99.9674
s = 0.0087		s = 0.0071

samples for each bottle are shown on the same line of the two corresponding sets.

The mean basimetric assay of this lot of tris is 99.9690 $\pm$ 0.0030 weight percent. The above uncertainty represents the 95-percent confidence interval for the mean. No evidence was found for variability between samples beyond that accounted for by the random error of measurement. Accordingly, the material is considered to be homogeneous. A pooled estimate of the random error (standard deviation of a single determination based on all 30 determinations) is 0.0081 assay units.

(G. Marinenko)

6. CONDUCTIMETRY

The Frequency Extrapolation of Conductance Data for Aqueous Salt Solutions

A. Introduction

Systematic sources of error in conductivity measurements are being sought as part of a program for standardizing and certifying solutions for use in the calibration of conductivity cells and salinometers. One such source of error is the frequency-dependent polarization impedance that inevitably accompanies the measurement of the ac conductance of solutions in conventional cells.

The present study deals with various mathematical means for extrapolating resistance vs. frequency data in order to remove polarization effects. Various experimental techniques for accomplishing the same objective were ruled out for reasons given below. Seven empirical and theoretical equations that have been used or proposed for the reduction of conductivity data are critically compared, using data for aqueous salt solutions in cells with bright platinum electrodes and with electrodes coated with palladium black. Robinson and Stokes [40] discuss polarization models qualitatively and emphasize that the functional form of the resistance-frequency curve must be determined whenever polarization is not negligible.

B. Test Equations

The equations to be compared and their historical or theoretical bases follow. R represents the observed resistance of a parallel R - C bridge arm having the same impedance as the conductivity cell, R_1 is the high-frequency limit of R (assumed to correspond to the electrolytic resistance of the cell), f is the frequency in Hz, and ω is the angular frequency ($2\pi f$).

1. Two-Parameter Equations

$$R = R_1 + a f^{-1/2} \quad (39)$$

Jones and Christian [41], in a classical study of polarization in conductivity measurements, recommended Eq. (39) as a practical expedient although it was recognized that this function led to R_1 values somewhat smaller than the true electrolytic resistance.

$$R = R_1 + a f^{-1} \quad (40)$$

Several workers [40,42] have found empirically that Eq. (40) better represented their data than did Eq. (39).

2. Three-Parameter Equations

$$R = R_1 + a f^{-1/2} + b f^{-1} \quad (41)$$

Nichol and Fuoss [43] found that the simpler Eqs. (39) and (40) were inadequate to represent their data for dipping electrode designs and used this quadratic function of $f^{-1/2}$.

$$R = R_1 + a f^b \quad (42)$$

Because of uncertainty as to the best exponent for f in Eqs. (39) and (40), Eq. (42) was proposed [44]. Although this equation can provide an excellent fit to experimental data, it will be seen below that it can introduce a large error in extrapolation. Accordingly, the use of Eq. (42) is not recommended.

3. Theoretical Equations

These are based on the model for the conductivity cell shown in Figure 13, where C_0 is the geometric capacity of the cell and C_1 is the double-layer capacity at the electrode surface. R_2 is the frequency-independent part of the faradaic impedance and W represents the Warburg impedance. The complex impedance of W is assumed to be represented by

$$Z_W = k(1 - i)\omega^{-1/2}. \quad (43)$$

R_2 arises from the rate of oxidation or reduction at the electrode and W from the diffusion of the electroactive species.

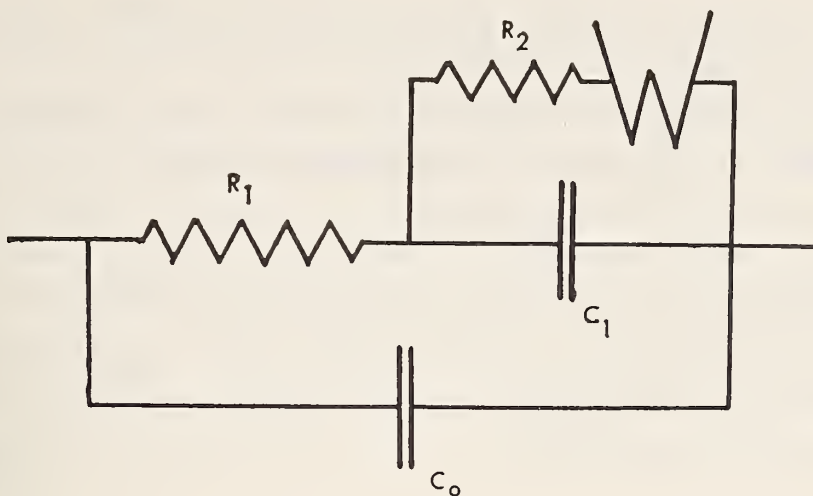


Figure 13. Equivalent circuit for conductance cell, according to reference 45.

Feates, Ives, and Pryor [45] solved the bridge balance conditions for this model with the restriction that W is negligible and obtained Eq. (44).

$$R = R_1 + \frac{R_2}{1 + a \omega^2} \quad (44)$$

where

$$a = R_1 R_2^2 C_1^2 / (R_1 + R_2). \quad (45)$$

These authors used an empirical extrapolation formula equivalent to Eq. (40) for reduction of their data.

The alternate solution for the model of Figure 13 for the simplifying condition that $R_2 = 0$ was given by Hills and Djordjevic [46]. Their corrected Eq. 4 in the notation of the present report is test Eq. (46).

$$R_s = R_1 + \frac{k}{\omega^{1/2} (1 + 2k C_1 \omega^{1/2} + 2k^2 C_1^2 \omega)} \quad (46)$$

Note that R_s is the resistance of an equivalent series R-C

bridge arm. The solution in terms of the parallel combination is much less tractable.

The bridge balance conditions for the model of Figure 13, including both the R_2 and Warburg impedance lead to the result [47]

$$R = R_1 + [R_2(R_1 + R_2) + k(R_1 + 2R_2)\omega^{-1/2} + 2k^2\omega^{-1}]/$$

$$[R_1R_2^2C_1^2\omega^2 + 2kR_1R_2C_1^2\omega^{3/2} + 2k^2R_1C_1^2\omega + 2kR_1C_1\omega^{1/2}$$

$$+ R_1 + R_2 + k\omega^{-1/2}]. \quad (47)$$

In order to fit Eq. (47) to experimental data it has been expanded in powers of $\omega^{-1/2}$ with the result

$$R = R_1 + a\omega^{-2} + b\omega^{-5/2} + c\omega^{-7/2} + \dots \quad (48)$$

where the coefficients have the theoretical values

$$a = (R_1 + R_2)/R_1R_2C_1^2 \quad (49)$$

$$b = -k/(R_2C_1)^2 \quad (50)$$

$$c = [2k^3R_1C_1 - 2kR_2(R_1 + R_2)]/R_1R_2^4C_1^3. \quad (51)$$

Because of the omission of higher negative powers of ω , Eq. (48) is expected to be asymptotically correct at higher frequencies.

Chang and Jaffe [48] examined the faradaic process in detail but did not obtain an explicit function for R in terms of f . Because of the difficulty of applying their results to conductivity data the Chang-Jaffe model is not considered further here.

The essential requirement of an extrapolation formula is that the high frequency limit R_1 correspond closely to the true resistance of the electrolyte in the cell. This condition was judged by the agreement between the value of R_1 obtained

for the same cell and solution whether the electrodes were bright platinum or coated with palladium black. The coating should change the double-layer parameters greatly without affecting R_1 . Since the palladium black has a finite thickness any effect on the cell constant was reduced by using capillary cells with relatively large constants (37 and 86). The extrapolation formula should also provide a close fit to the experimental measurements over an appreciable range of frequencies. It is also desirable that the theoretically based equations yield plausible values for the double-layer parameters.

Although the use of platinum or palladium black is a familiar and effective means of reducing polarization effects on conductivity measurements, bare metallic electrodes have some advantages for checking standard solutions. We prefer to introduce the sample to a clean, dry cell when only a limited specimen is available since there may not be enough to rinse the cell to constant composition as would be required with the highly adsorptive blacked electrodes. Potentiometric [49] and inductive [50] cells have been used to avoid polarization effects completely but these require specialized measuring instruments and are not suitable to our ultimate objective of redetermining the Jones and Bradshaw [51] standards on an absolute basis.

C. Experimental Section

1. Apparatus

Two cells of the conventional Jones design were used. These had circular platinum electrodes 7.0 square centimeters in area in enlarged bulbs connected by a sufficient length of 4-mm i.d. tubing to give constants of 37.050 and 86.096. Two bare copper leads were soldered to each electrode support close to the outside of the cell for use with the four-terminal method of measurement. The uncompensated lead resistance was calculated from the materials of construction (copper, tungsten,

and platinum) to be 0.002 ohm.

A Jones-Dike bridge was modified for use in the four-terminal mode by providing auxilliary switches for reversing leads and connecting the active potential lead directly to the detector. In this configuration the entire slide-wire circuit of the bridge was in the "Standard" arm and 26.181 ohms was determined to be the correction to be added to the dial readings to compensate for this modification.

The parallel capacitance required for balance was provided by an external calibrated 1400 pF variable air capacitor, supplemented as needed by mica capacitors up to 0.06 μ F. The thermostat was a self-lagging oil bath equipped with proportional, rate, and reset controls. Temperatures were measured with two calibrated platinum resistance thermometers of different time constants (6 and 11 seconds). In 28 measurements the maximum difference between the readings of the two thermometers was 3.6×10^{-3} K, while the standard deviation of the difference was 1.6×10^{-3} K and the mean difference was less than one-fifth the standard deviation.

2. Solutions and Filling of Cells

Two solutions were used: demal potassium chloride [51] sealed in 100-cm³ ampoules and Standard Sea Water, Lot P50, which is supplied in double-necked 250-cm³ ampoules [52]. Our experience has confirmed the observation that a major source of random error is in the filling of cells [53]. We have obtained standard deviations less than 50 ppm for the measurement of conductivities of sets of four or five ampoules of Standard Sea Water and attribute the high degree of precision largely to the ability to drain the sample directly from the ampoule into the cell. The potassium chloride solution was prepared from specially purified and dried salt and contained 71.1435 grams of KCl per kilogram of solution (corrected to vacuum weights). Borosilicate ampoules were filled in a 5 °C cold room, having first been flushed with nitrogen presaturated

with the same solution. The filled ampoules were immersed in an ice bath above the solution level while the necks were sealed off.

Cells with bright electrodes were rinsed thoroughly with distilled water, followed by three portions of spectrographic grade acetone, dried with nitrogen and filled from freshly opened ampoules. At the end of this series of measurements, each electrode was palladized for 4.5 minutes at 50 mA, using a solution prepared by electrolytically dissolving 0.1 g of palladium in 20 cm³ of constant-boiling hydrochloric acid and diluting to 100 cm³. Palladium black is advantageous in that it can be stripped completely from the electrode. The coated electrodes were rinsed thoroughly and electrolyzed in dilute sulfuric acid for 1.5 hours with frequent reversals of polarity. The palladized electrodes were never allowed to become dry but were kept wet with water or aqueous electrolyte. Before filling, the cells were rinsed several times with a solution of the approximate composition as that to be measured, and finally with a small portion from the freshly opened ampoule. After the resistance measurement the cell was emptied and immediately refilled from another ampoule of the same solution and the measurements were repeated. The resistances for the second series were 0.01 to 0.07 percent lower than the first and are the ones reported here.

3. Fitting Equations to Data

After applying bridge calibration corrections and adjusting the data to exactly 25 °C (on the International Temperature Scale of 1948), the seven equations were fitted by computer programs. The linear equations (39 and 40) were fitted by conventional least square methods. The polynomials of degree higher than first (Eqs. 41 and 48) were fitted by orthogonal polynomials [54]. The non-linear forms (Eqs. 42, 44, and 46) were fitted by an iteration technique that varied one parameter until the sum of the squares of deviations was minimized. For each value of the independently adjusted parameter the other

two parameters were set by a least-squares fit of a linearized form of the equation. The step size for the iteration was varied in a way that guaranteed that the sum of squares of deviations passed through the minimum at least once and convergence was accepted when successive iterations reduced the sum of squares less than 0.01 percent.

D. Results and Discussion

The results [47] are summarized in Table 19, where the calculated values of R_1 according to the seven equations are compared for two solutions and two cells, each with bright and with palladized electrodes. With respect to the requirement that the equations yield the same value for R_1 for either bright or coated electrodes, both theoretical Equations (44) and (48) are very satisfactory. The relative differences for all eight comparisons are less than 70 ppm. That these values of R_1 represent the true resistance of the electrolyte is supported by not only the prediction from the theoretical models, but also by the fact that nearly all the extrapolation formulas yield the same results for the palladium blacked electrodes. A notable exception is the exponential Equation (42) in the case for the cell (constant 37) with demal potassium chloride. Here the best fit yielded a large exponent ($b = -1.47$) and a value of R_1 some 70 ohms too low.

The simple, two-parameter equation in reciprocal frequency (Eq. 40) provides very satisfactory agreement between the measurements obtained with bright and coated electrodes but this agreement appears to be the result of a cancellation of errors. The comparison of several of these functions in Figure 14 shows that Equation (40) actually reproduces the experimental data quite poorly. Over a limited range of frequencies (approximately 1 to 10 kHz) a good fit can be obtained with Equation (40) but it then extrapolates to too low a value for R_1 .

Table 19. Limiting resistance R_1 and standard deviation of fit for seven test equations applied to experimental data

		Cell constant 37				Cell constant 86			
		KCl		SSW		KCl		SSW	
		bright	coated	bright	coated	bright	coated	bright	coated
Freq. range (kHz)		0.25-15.0	0.25-10.0	0.25-15.0	0.25-10.0	0.25-10.0	0.25-8.0	0.25-10.0	0.25-2.0
Eq. 39									
R_1		332.422	332.875	697.539	698.255	773.116	773.411	1621.37	1621.98
s.d.	a	0.046	0.007	0.161	0.004	0.029	0.006	0.13	0.005
Eq. 40									
R_1		332.902	332.885	698.172	698.263	773.474	773.423	1621.90	1621.99
s.d.		0.141	0.009	0.073	0.003	0.10	0.007	0.10	0.005
Eq. 41									
R_1		332.480	332.859	698.006	698.260	773.102	773.408	1621.701	1621.99
s.d.		0.038	0.005	0.049	0.003	0.026	0.005	0.075	0.004
Eq. 42									
R_1		332.597	262.640	698.134	698.258	773.143	773.370	1621.871	1621.99
s.d.		0.039	0.005	0.058	0.003	0.027	0.005	0.091	0.004
Eq. 44									
R_1		332.895	332.874	698.277	698.265	773.457	773.421	1621.921	1621.99
s.d.		0.067	0.005	0.058	0.004	0.046	0.006	0.048	0.005
Eq. 46									
R_1		332.644	332.875	697.922	698.264	773.151	773.421	1621.79	1622.00
s.d.		0.036	0.006	0.020	0.003	0.038	0.001	0.06	0.002
Eq. 48									
R_1		332.872	332.883	698.227	698.264	773.434	773.421	1621.931	1621.99
s.d.		0.047	0.008	0.015	0.004	0.037	0.007	0.021	0.007

^aThe square root of the mean squared difference between experimental and calculated resistance is designated by s.d. (ohms).

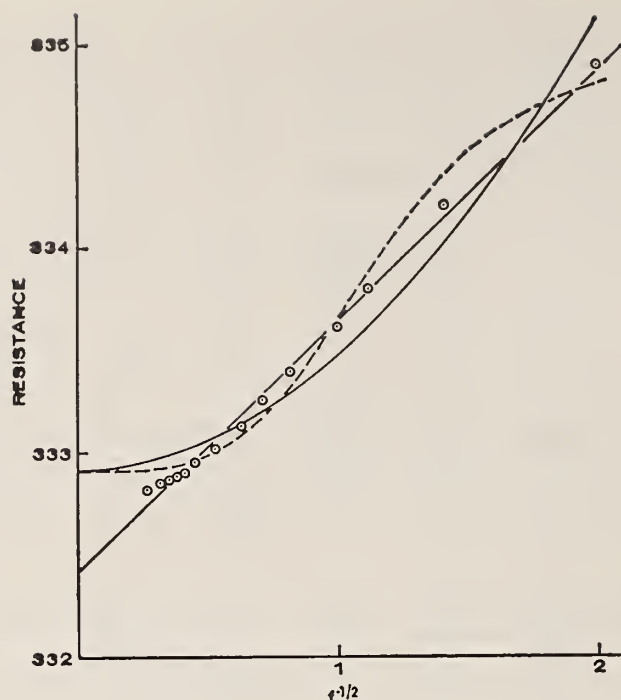


Figure 14. Comparison of test equations. Data points are for demal KCl, bright platinum electrodes, cell constant 37.

Key: Equation 39, straight line; 40, solid curve; 44, broken curve.

The equations that provide the best extrapolation do not necessarily fit the data most closely. In Figure 15, deviations from Equation (44) are plotted as a function of $f^{-1/2}$. This scale expands the high frequency region where the extrapolation behavior is crucial. It appears that none of the functions fits the data within experimental precision although Equation (41) gives the smallest standard deviation of fit (Table 19). Equation (42) yields essentially the same result as Equation (41). It is well known that the close fit of an empirical equation to a set of data does not provide a sound basis for extrapolating beyond the range of the measurements and this caution applies to the four empirical forms considered in the present report.

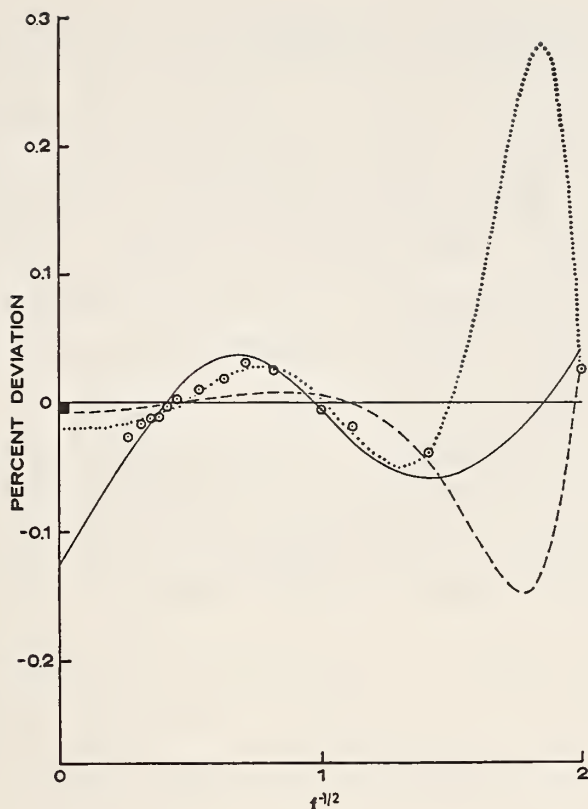


Figure 15. Percentage deviations from test equation 44. Data points are for demal KCl, bright platinum electrodes, cell constant 37. The solid rectangle at the origin of the coordinates represents the probable limiting resistance for palladized electrodes.
Key: Equation 41, solid; 48 broken; 48 plus next higher term dotted.

Equation (46) has not been mentioned in the foregoing discussion because it was not tested on a strictly comparable basis. The measurements were made with a parallel R-C bridge arm and had to be recalculated to the equivalent series values by Equations (52) and (53) in order to apply Equation (46).

$$R_s = R_p / (1 + \omega^2 R_p^2 C_p^2) \quad (52)$$

$$C_s = C_p [1 + 1/(\omega^2 R_p^2 C_p^2)] \quad (53)$$

Capacitances were measured with much less accuracy than resistances and the application of Equations (52) and (53) introduced an undetermined error. Although Equation (46) is a fit of R_s vs. ω , points were omitted when the corresponding value of the series capacitance appeared clearly discordant. Equation (46) reproduces the data points more closely than Equation (44) but extrapolates to R_1 values that seem uniformly nearly 0.2 ohm too low. These functions (Eqs. 44 and 46) are compared in Figure 16.

It is apparent from Figure 15 that Equation (48) behaves very poorly at the lower frequencies, probably due to the neglect of higher terms in the polynomial expansion of Equation (47). The next higher term is $d \omega^{-4}$, where

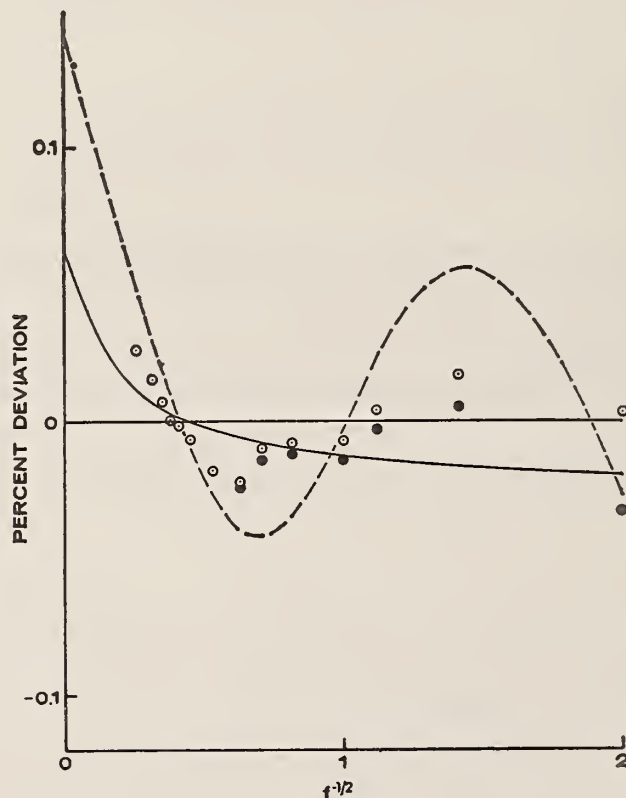


Figure 16. Percentage deviations from test equation 39. Data points are for demal KCl, bright platinum electrodes, cell constant 37.
Key: R_p , open circles; R_s , filled circles; Equation 44, broken line; 46, solid curve.

$$d = - \frac{4k^4}{R_2^5 C_1^2} - 2k^2 \frac{(3R_1 + R_2)}{R_1 R_2^4 C_1^3} + \frac{(R_1 + R_2)^2}{R_1^2 R_2^3 C_1^4} . \quad (54)$$

Inclusion of the term in ω^{-4} improves the fit appreciably reducing the standard deviation from 0.047 to 0.015 ohm. However, the behavior between the two lowest experimental frequencies is even more extreme, as shown in Figure 15.

The fundamental parameters of the faradaic impedance and double layer for the theoretical models are compared in Table 20. The parameters are at least plausible in magnitude although it is questionable how much physical significance should be attached to them. The coefficients for one example are shown in Table 21. Their standard deviations are sufficiently

Table 20. Fundamental parameters of conductance cell derived from frequency dependence of resistance

Demal KCl, bright platinum electrodes, cell constant 37

	Eq. 44	Eq. 46	Eq. 48	48 plus higher term
R_1 (ohm)	332.895	332.644	332.872	332.826
R_2 (ohm)	2.107	---	8.44	4.17
C_1 (μ F)	102.8	15.58	35.3	34.5
k (ohm-sec $^{-1/2}$)	---	96.3	476	324

Table 21. Polynomial coefficients and their standard deviations.

Test equation 48 fitted to data for demal KCl, bright platinum electrodes, cell constant 37.

	4-term eq.	5-term eq.
Const.	332.872 ± 0.019	332.828 ± 0.008
2nd	$(97.6 \pm 7.8) \times 10^6$	$(20.4 \pm 1.2) \times 10^7$
3rd	$-(58.1 \pm 5.7) \times 10^8$	$-(18.2 \pm 1.3) \times 10^9$
4th	$(33.6 \pm 4.2) \times 10^{11}$	$(41.9 \pm 4.1) \times 10^{12}$
5th	---	$-(10.2 \pm 1.1) \times 10^{14}$

large to suggest considerable uncertainty in any derived parameters. It is interesting that the inclusion of an additional term to Equation (48) greatly changes the polynomial coefficients but appreciably affects only the R_2 parameter.

E. Recommendations

Although the frequency dependence of the measured resistance should be determined when polarization is not negligible, this step is not sufficient to insure accuracy. The Grahame model of Figure 13 and its simplifications predict that the limiting resistance is approached horizontally. Consequently, any of the simple extrapolation formulas that have been proposed will give low results. In many cases, an experimental value in the range 5 to 10 kHz is more accurate than an empirical extrapolation. Either Equation (44) or (46) is sufficiently accurate for extrapolation purposes. These equations are solved by essentially the same program and the choice depends upon the experimental set-up accordingly as the equivalent parallel or series R-C combination is measured. In solution conductivity work, it is usually preferable to use the parallel configuration in order to avoid the need for large capacitors.

(T. B. Hoover)

7. FOREIGN-CURRENCY PROGRAMS

The two projects, sponsored by the Electrochemical Analysis Section at universities in India and financed through the provisions of Public Law 480, continued actively during the reporting year. A brief description of these programs follows.

A. Properties of Electrolytes in Nonaqueous Media, Dr. M. N. Das and Dr. K. K. Kundu, Jadavpur University, Calcutta

(1) Studies on the behavior of some uncharged bases in aquo-glycolic and aquo-methanolic solvent systems.

(2) Standard potentials of Li/Li^+ and Cs/Cs^+ electrodes in ethylene glycol-water systems.

(3) Acidity function (H_-)^{Eg} for solutions of sodium and lithium glycoxides in ethylene glycol at 25°C.

(4) Studies in isodielectric media: standard potentials (E_m°) of Ag-AgCl electrode in methanol-propylene glycol solvent system at different temperatures and the related thermodynamic quantities.

Publications resulting from the above programs are:

K. K. Kundu, D. Jana, and M. N. Das, "Standard Potentials of the Silver-Silver Bromide Electrode in Propylene Glycol and the Silver-Silver Iodide Electrode in Ethylene and Propylene Glycols at Different Temperatures and Related Thermodynamic Quantities", J. Phys. Chem. 74 (13), 2625 (1970).

K. K. Kundu, P. K. Chattopadhyay, D. Jana, and M. N. Das, "Thermodynamics of Self-Ionization of Ethylene and Propylene Glycols", J. Phys. Chem. 74 (13), 2633 (1970).

K. K. Kundu, P. K. Chattopadhyay, D. Jana, and M. N. Das, "Standard Potentials of Ag-AgX (X = Cl or Br) Electrodes in Glycolic Solvents at Different Temperatures and Related Thermodynamic Quantities", J. Chem. Eng. Data 15, 209 (1970).

B. Physicochemical Studies in Nonaqueous Solvents, Prof. R. C. Paul, Panjab University, Chandigarh

Recent work is described in the following manuscripts:

R. C. Paul, D. S. Gill, and S. P. Narula,
"Physicochemical Studies in Nonaqueous Solvents.
Part I. Conductance and Thermochemical Studies
of Some Perchlorates in N,N-Dimethylformamide",
J. Chem. Soc. (A) (in press).

R. C. Paul, D. S. Gill, J. P. Singla, and S. P.
Narula, "Physicochemical Studies in Nonaqueous
Solvents. Part II. Conductance and Solvation
Studies in N-Methylformamide", J. Phys. Chem.
(submitted).

(R. A. Durst)

8. PERSONNEL AND ACTIVITIES

A. Personnel Listing

Richard A. Durst, Acting Section Chief

Carolyn E. Smith, Section Secretary

Acidity Scales --

Maya Paabo

Conductimetry --

Thomas B. Hoover (to January 1970)

Coulometry --

George Marinenko

Ion-Selective Electrodes --

Bert R. Staples

Robert G. Hayman (Guest worker September to February)

Duane Wood (Guest worker February to June)

Potentiometry --

Benjamin T. Duhart (part time)

Consultant --

Roger G. Bates

B. Publications and Manuscripts

1. R. G. Bates, "Solute-Solvent Interactions" in Medium Effects and pH in Nonaqueous Solvents, Marcel Dekker, New York, 1969, pp. 45-96.
2. M. Paabo and R. G. Bates, "Dissociation of Deuterio-carbonate Ion in Deuterium Oxide from 5 to 50°", J. Phys. Chem. 73, 3014 (1969).
3. R. A. Robinson, "An Isopiestic Vapor Pressure Study of the System Potassium Chloride-Sodium Chloride in Deuterium Oxide Solutions at 25°", J. Phys. Chem. 73, 3165 (1969).

4. R. A. Durst, "Fluoride Microelectrode--Fabrication and Characteristics", Anal. Chem. 41, 2089 (1969).
5. R. G. Bates, Editor, NBS Technical Note 503, "Electrochemical Analysis Section: Summary of Activities, July 1968 to June 1969", U. S. Government Printing Office, August 1969.
6. R. G. Bates, "Proposal for the Practical Measurements of pH in Amphiprotic and Mixed Solvents", Pure & Appl. Chem. 18, 419-425 (1969).
7. G. Marinenko and C. E. Champion, "Difference between the Inflection Point and the Equivalence Point in Coulometric Titrations of Weak Acids", Anal. Chem. 41, 1208 (1969).
8. R. G. Bates and M. Alfenaar, "Activity Standards for Ion-Selective Electrodes", in Ion-Selective Electrodes, NBS Special Publication 314, U. S. Government Printing Office, 1969, p. 191.
9. R. A. Durst, "Analytical Techniques and Applications of Ion-Selective Electrodes" in Ion-Selective Electrodes, NBS Special Publication 314, U. S. Government Printing Office, 1969, p. 375.
10. R. A. Durst, Editor, Ion-Selective Electrodes, NBS Special Publication 314, U. S. Government Printing Office, 1969.
11. R. G. Bates, B. R. Staples, and R. A. Robinson, "Ionic Hydration and Single Ion Activities in Unassociated Chlorides at High Ionic Strengths", Anal. Chem. 42, 867 (1970).
12. M. Paabo and R. G. Bates, "Dissociation Constant of Protonated 2,2-Bis(hydroxymethyl)-2,2',2"-nitrilotriethanol (Bis-tris) and Related Thermodynamic Functions from 0 to 50°", J. Phys. Chem. 74, 702 (1970).
13. M. Paabo and R. G. Bates, "Deuterium Isotope Effects and the Dissociation of Deuteriophosphoric Acid from 5 to 50°", J. Phys. Chem. 74, 706 (1970).
14. E. J. Catanzaro, C. E. Champion, E. L. Garner, G. Marinenko, K. M. Sappenfield, and W. R. Shields, "Boric Acid; Isotopic and Assay Standard Reference Materials". NBS Special Publication 260-17, U.S. Government Printing Office, 1970.
15. R. A. Robinson, "The Dissociation Constant of m-Nitro-anilinium Ion in Water-Tetrahydrofuran Solvents at 25 °C", J. Res. NBS (in press).

16. M. Paabo and R. G. Bates, "Acidic Dissociation of Diprotonated Piperazine in Methanol-Water Solvents from 10 to 40 °C", J. Res. NBS (in press).
17. R. A. Durst and B. T. Duhart, "Ion-Selective Electrode Study of Trace Silver-Ion Adsorption on Selected Surfaces", Anal. Chem. (in press).
18. H. P. Thun, B. R. Staples, and R. G. Bates, "Thermodynamics of Hydrochloric Acid in 80 Weight Percent 2-Methoxyethanol and 20 Weight Percent Water from 10 to 50 °C", J. Res. NBS (in press).
19. T. B. Hoover, "Frequency Extrapolation of Conductance Data for Aqueous Salt Solutions", J. Phys. Chem. (in press).
20. R. A. Robinson, "The System: Potassium Chloride-Sodium Chloride in Deuterium Oxide Solution at 25°", J. Phys. Chem. (submitted).
21. R. A. Durst, "Ion-Selective Electrodes in Science, Medicine, and Technology", Amer. Scientist (submitted).

C. Talks

1. G. Marinenko, "Coulomb - the Absolute Chemical Standard", The American University, Washington, D. C., September 22, 1969.
2. R. A. Durst, "Ion-Selective Electrodes", NBS Analytical Chemistry Division Scientific Discussion, October, 1969.
3. M. Paabo, "Thermodynamics of the Dissociation of Protonated Bis-Tris from 0 to 50 °C", Southeastern Regional Meeting, American Chemical Society, Richmond, Virginia, November 1969.
4. R. A. Durst, "Microanalysis Using Ion-Selective Electrodes", Southeastern Regional Meeting, American Chemical Society, Richmond, Virginia, November 1969.
5. T. B. Hoover, "Frequency Extrapolation of Conductance Data for Aqueous Solutions, Southeastern Regional Meeting, American Chemical Society, Richmond, Virginia, November 1969.
6. R. G. Bates, "Proton Medium Effects and the Measurement of Acidity in Nonaqueous and Mixed Solvents", Eastern Analytical Symposium, New York, New York, November 1969.

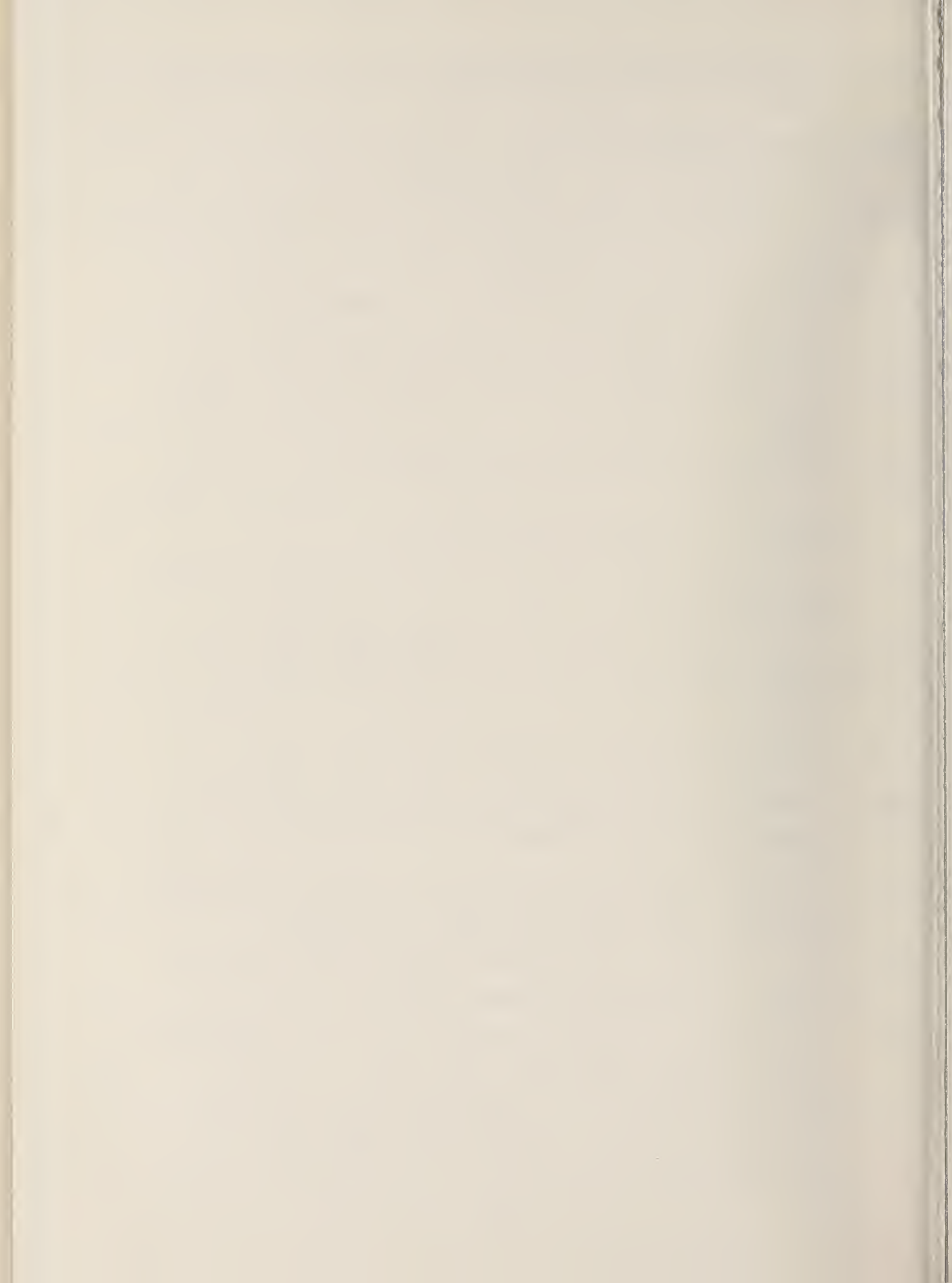
7. R. A. Durst, "Ion-Selective Electrodes and Their Applications", Analytical Section, New York Chemical Society, New York, New York, January 1970.
8. R. A. Durst, "Electrochemical Analysis Capabilities in Chemical Oceanography" (panel), NBS Analytical Chemistry Division Scientific Discussion, January 1970.
9. G. Marinenko, "Ion-Selective Electrodes", Department of Chemistry, The American University, February 1970.
10. R. A. Durst, "Ion-Selective Electrode Study of Trace Silver Adsorption on Selected Surfaces", 159th National Meeting, American Chemical Society, Houston, Texas, February 1970.
11. R. A. Durst, "Ion-Selective Electrodes in Science, Medicine, and Technology", Sigma Xi National Lecture Tour, New York area, March 9-19, 1970.
12. M. Paabo, "Acid-Base Behavior of Piperazinium Ion in Methanol-Water Solvents", Fifth Middle Atlantic Regional Meeting, American Chemical Society, University of Delaware, Newark, Delaware, April 1970.
13. B. R. Staples, "Thermodynamics of Hydrochloric Acid in a Mixed Solvent Containing 80 Weight Percent 2-Methoxyethanol and 20 Weight Percent Water from Emf Measurements at 10 to 50 °C", Fifth Middle Atlantic Regional Meeting, American Chemical Society, University of Delaware, Newark, Delaware, April 1970.
14. R. A. Durst, "Ion-Selective Electrode Studies at NBS", Chemistry Department Colloquium, University of Connecticut, Storrs, Connecticut, May 1970.
15. M. Paabo, "Acid-Base Behavior of Piperazinium Ion in Methanol-Water Solvents", Joint Meeting of the Canadian Institute of Chemistry and the American Chemical Society, Toronto, Canada, May 1970.
16. R. A. Durst, "Ion-Selective Electrodes", Food and Drug Administration, U. S. Department of Health, Education, and Welfare, Washington, D. C., June 1970.
17. R. A. Durst, "Analytical Applications of Ion-Selective Electrodes", 23rd Annual Summer Symposium on Analytical Chemistry, American Chemical Society, New Mexico State University, Las Cruces, New Mexico, June 1970.

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